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STANDARD TABLE
OF
ELECTROCHEMICAL EQUIVALENTS
AND
THEIR DERIVATIVES

Standard Table
OF
ELECTROCHEMICAL EQUIVALENTS
AND
Their Derivatives

WITH
Explanatory Text on Electrochemical Calculations
Solutions of Typical Practical Examples and
Introductory Notes on Electrochemistry

BY
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AND

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PREFACE

The chief purpose of this publication is to serve as a reference book on account of the tables and other data given in it, and not as a treatise on electrochemistry in general; sufficient explanatory text has however been added to enable the data to be used for most purposes without the need of a further treatise on the subject. To make the data available also to the student, electroplater, engineer, and others who may not have made a special study of chemistry and electrochemistry, the descriptive text has been given in elementary and easily understood terms.

In *Electrochemical Industries* (later *Metallurgical & Chemical Engineering*) for January, 1903, one of the present authors, Carl Hering, published a very complete table of electrochemical equivalents calculated from the then best fundamental values. Since then a more accurate value of the fundamental electrochemical constant, based on silver, has been adopted internationally and quite a number of the atomic weights have been changed. The table in the present book has therefore been entirely recalculated by its author from the latest and best internationally adopted fundamental values, including the atomic weights for 1917. It has also been enlarged to include all the elements and practically all of their valences. The equivalents are given in terms of various units, including in each case their reciprocals.

The methods of making electrochemical calculations involving these equivalents are described by means of a number of typical practical examples accompanied by explanatory notes. A brief description of some of the elementary principles of chemistry involved in such calculations, has been added.

Some of the conceptions and simplified methods of calculation described in the text may differ from those more generally taught or found in textbooks; they are offered here merely as suggestions which lead to the same result as the older and more complicated ones; the latter are also described as alternatives to be used by those who prefer them.

The rapid developments of recent years in the physical conceptions of electrochemical phenomena made it desirable to include an introductory description of them in a section on the Electronic Theory. This, and a section on Electrolysis which includes a brief explanation of the dissociation theory, have been prepared by the other author, Frederick H. Getman.

The authors acknowledge their indebtedness to Dr. J. W. Richards for revising and bringing up to date his table of the valences which the elements have in their more usual combinations. Also to the Bureau of Standards for most of the fundamental constants and for valuable advice and assistance.

CARL HERING
FREDERICK H. GETMAN

Philadelphia, Pa., and Stamford, Conn.,
June, 1917.

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INTRODUCTION

The chief purpose of the present book is to provide a table of constants, based on the latest and best fundamental values, for making calculations of the amounts of substances electrolytically deposited, dissolved, or otherwise chemically changed, by an electric current, and to explain by means of a series of typical practical examples and descriptive text, how such calculations are made. This forms Part I.

In many of the simplest kinds of calculations involving merely the quantities of metal deposited or dissolved, or the quantities of gases evolved by a given current, or the reverse, the calculations by means of the constants in the table are so extremely simple, consisting merely of a multiplication, that no further knowledge of chemistry or the laws of electrolysis is required, all the involved parts of the complete calculations having been made in the preparation of the table.

Many of these calculations being greatly simplified by considering the chemical valence as a separate factor, as distinguished from using chemical equivalents, a description of the significance which the valences have in electrochemistry is given in Appendix I; the application of valences to such calculations is described in the examples. The older methods are also described for the benefit of those who do not understand or do not agree with the suggested conception of the meaning and application of valence to electrochemical calculations which is believed to be in agreement with the modern and generally accepted electronic theory.

The physical conception of electrochemical phenomena has been greatly developed in recent years, and altho this does not change the simplest ways of making the calculations by the use of this table, yet it is of interest and of use. This has been briefly summarized in Part II, which includes also a brief treatise on electrolysis as based on the modern dissociation theory.

The elementary principles of chemistry involved in the usual calculations are briefly summarized in Appendix II; for the more involved cases a further knowledge of chemistry and electrochemistry is necessary.

A list of the principal conversion factors[1] used in such calculations is given in Appendix III.

In place of a glossary of the terms used in this book, the places in the text where they have been defined and used are given in Appendix IV.

---

[1] Taken from Hering's Conversion Tables.

PART I

Section I

FUNDAMENTAL LAWS

The simplest and most basic law of electrolysis refers to the elements when they are in their gaseous state, or in the state of vapor. When in this state it is true alike for every element that to set free a liter of this gas or vapor requires the same constant amount of electricity in coulombs or ampere-hours when there is one atom to the molecule and when the change of valence is unity. For those elements in which there are two or more atoms to the molecule it will require two or more times this constant quantity of electricity, in direct proportion; and for any other change of valence the constant must also be increased in direct proportion. This law applies strictly to perfect or ideal gases only, and it may be true that some of the gaseous elements deviate slightly from this perfect state; the latter may be due to a lack of precision in our knowledge of the physical constants of the elements in their gaseous form. But the deviations do not seem to be greater than fractions of one percent and they may therefore be neglected in most cases.

From the latest and best fundamental physical constants, which are given in Section II, this fundamental constant for perfect gases is 4,309.7 coulombs, or 1.1971 ampere-hours, per liter of gas or vapor, at 0°C. and 760 mm. atmospheric pressure; or exactly 1 ampere-hour per liter at a temperature of 53.82° C. The fifth place of figures is uncertain. This constant applies directly to a monatomic element (meaning one having only one atom to the molecule) like sodium vapor for instance, when the change of valence is unity; for a diatomic element (two atoms to the molecule) like hydrogen, and when the change of valence is unity, this constant must be multiplied by 2; for a diatomic element like oxygen, and when the change of valence is 2 (the element is then called bivalent or di-valent) the constant must be multiplied by 2×2; etc.

As this constant is the same for all the elements and is independent of their atomic weights or vapor densities, this relation between the amount of gas or vapor and the amount of electricity required to set it free is the simplest and most direct one, and may therefore be said to be the most fundamental one. It may be said to be the physical relation as distinguished from the chemical relation more commonly used. It may be deduced by combining the generally accepted law of Faraday with that of Avogadro, which latter states that one gram molecule of every element occupies the same volume when it is in its state of gas or vapor, when the temperatures and pressures are the same.

When the amounts of electrolytic gases of any of the elements are desired in terms of their volume, as distinguished from their weight, this relation is also the simplest and most direct one to use for making the calculations; and as it happens that all the six gaseous elements which might be evolved electrolytically are diatomic at ordinary temperatures, doubling this constant will make it apply to all of them for each unit change of valence. Derivatives of this constant, for convenience in calculations concerning these six elements, are given in Table III.

But in most cases the elements concerned in electrolytic calculations are not in their gaseous state and sometimes they merely undergo a chemical change and are not set free or dissolved. This simple physical relation is then not the most convenient one to use. Moreover to specify a quantity of a substance in terms of its weight (or mass) instead of its volume, is often the most rational way, and may simplify other subsequent calculations; for gases furthermore the quantity is then independent of the otherwise disturbing effect of the temperature and pressure.

When the weights of the quantities are concerned the simplest relation, deduced from Faraday's law, is that every gram ion involved in an electrolytic change, no matter of which element, requires the same number of coulombs or ampere-hours of electricity, per unit change of valence; if the change of valence is two, three, etc., the amount of electricity is two, three, etc., times as great.

From the latest and best fundamental physical constants given in Section II, this constant is 96,494 coulombs or 26.804 ampere-hours per gram ion. This is called a "faraday," a name which has not yet been formally adopted but is sanctioned by good usage and has been generally accepted. For many calculations however this constant is a very inconvenient and awkward one to use; the following derivatives of it will often be found more convenient. Table I is based on this constant.

The quantity of electricity required to electrolyze a given quantity of any element *by weight*, and fo each unit change of valence, is equal to:

96.494 ÷ atomic weight, in coulombs per milligram;
26.804 ÷ atomic weight, in ampere-hours per gram;
12,158. ÷ atomic weight, in ampere-hours per pound.

The reciprocals of these standard values are:

Atomic weight × 0.010363, in milligrams per coulomb;
Atomic weight × 0.037308, in grams per ampere-hour;
Atomic weight × 0.082250, in pounds per 1000 ampere-hours.

The physical meaning of these constants is that they would be the actual values for a hypothetical element having an atomic weight of exactly unity. As the atomic weight of hydrogen is 1.008 they represent that element to within a little less than 1%.

These constants are for a change of valence of unity; when it is other than unity those of the first group must be multiplied by the change of valence, or those of the second group (the reciprocals) divided by it.

The term "change of valence" is used here instead of the shorter one "valence" used in most books, because the latter term by itself may sometimes lead to very incorrect results; it is not always the valence which an element has in a chemical compound which governs the electrolytic quantities involved, but it is always the *change* of valence during electrolysis which is the true governing factor, that is, it is always the *difference* between the valences before and after electrolysis. Faraday's law stated in terms of valence, as it usually is, fails to apply in some cases, but when stated in terms of the change of valence it becomes a universal law.

The valence of any element in its free, uncombined state must be considered to be zero, because the term valence, in Faraday's law at least, must be interpreted to mean the number of bonds per atom which hold it in combination with another element, hence when the element is no longer combined these bonds of course no longer exist. Therefore when an element has been set free by electrolysis it means that it has changed its valence from what it had in the compound to zero; in that specific case therefore, and only in that case, is the "valence" numerically equal to the "change of valence," and it is only this particular case and not the more general one, that the textbooks can refer to when they give Faraday's law in terms of "valence" instead of more broadly and more correctly in terms of the "change of valence." For further explanations see the examples in Section IV and Appendix I on Valence.

It follows from the above that the same current will electrolyze chemically equivalent quantities per minute. For some cases this is a convenient way of stating Faraday's law; the valence then does not enter into the calculation as it is already embodied in the chemically equivalent quantities. This is illustrated in the examples, Section IV.

Another fundamental law of electrolysis is that at the cathode there will always appear that kind of a chemical reaction which is called a reduction, which always involves a reduction of the valence, while at the anode there will always appear the opposite or reversed kind called oxidation, or better, adduction, which always involves an increase of valence. When chemical reductions and adductions or oxidations are thus interpreted in terms of changes of valence, for simplifying conceptions and calculations, it becomes necessary to couple with the valence the algebraic signs + or – which it must have in order to correspond with the direction of the current which produces the reaction. For further explanation see Appendix I on Valence.

Section II

FUNDAMENTAL DATA AND DESCRIPTION OF THE TABLES

The fundamental constants on which the values in this table are based are the electrochemical equivalent of silver, 0.001 118 00 gram per coulomb, which has been accepted internationally, and the atomic weight of silver 107.88 which is the internationally accepted value for 1917. Both have been accepted by the Bureau of Standards.

Their quotient gives the resulting value 96 493.7 coulombs per univalent gram ion (log = 4.984 4991) for the electrochemical constant called the faraday; for most purposes this is more conveniently rounded off to 96 500, the error being less than 1/100 of 1 %. The equivalent of the former is 26.803 8 ampere-hours (log = 1.428 1966), conveniently rounded off to 26.8 (error about 1.5 hundredths of 1 %). On the above basis the faraday necessarily becomes a derived quantity and is therefore not the fundamental constant.

The atomic weights of all the elements are the international values for 1917, based on oxygen = 16, but as the electrochemical equivalents are absolute and not relative, they would of course be the same for atomic weights based on hydrogen = 1. These atomic weights were obtained directly from Dr. F. W. Clarke, Chairman of the International Committee. The table includes the constants for all the elements excepting only the six noble gases which enter into no combinations.

Altho most of the atomic weights are not known to more than four places of figures, the constants in the table have been carried out uniformly to five places in order that when more accurate atomic weights become known the constants can be corrected by proportion. In order that all calculations may be made by a multiplication, the reciprocals of all the values have also been given, thereby eliminating all calculations by division. The constants are given in terms of the three most commonly used compound units, milligrams per coulomb, grams per ampere-hour and pounds per 1000 ampere-hours.

The different valences for which the constants are given in Table I are believed to include most of the cases occurring in practice, either as valences or as changes of valences. In some cases the constants for a valence 1 have been included even tho that valence may not occur in practice, in order to facilitate calculating the constants for other valences or changes of valence than those given, by a mere multiplication or division by the new valences; to avoid confusion these values are italicized in Table I. Near the end of this table it is shown how to calculate the constants for any other valences; thus if n is the constant given in any of the columns for a valence v, then for any other valence x multiply the constant n by v/x or by x/v as stated in that column. For the valences which the elements have in their various compounds see Table IV.

The last line of values gives the general formulas and constants for calculating any of the values in the table for any atomic weight y and any valence x, based on the internationally accepted fundamental electrochemical equivalent as given above.

Table II gives the constants of column 7 of Table I, arranged in the order of the magnitude of the electrochemical equivalents of the elements. For other valences than those given in the table there would of course be additional values in this supplementary table. The values given in italics in Table I have been omitted in Table II.

The constants in Table I are in terms of the *weights*, but when the *volumes* are desired of those elements which are gases, the calculations of the amounts set free by electrolysis are still further simplified by using the constants in Table III; it being then a physical as distinguished from a chemical relation, the constants become the same for all the gaseous elements, as they no longer involve the atomic weights; this follows from a combination of the laws of Faraday and Avogadro. This relation is accurately true only for perfect gases; slight deviations may therefore arise in practice. The additional basic constant involved in the determinations of the conversion factors in this Table III is the constant of Avogadro's law, namely 22.390 liters, for the volume of a gram molecule of any of the elements in their gaseous state, at 0° C and 760 mm. This constant is here deduced from the weight of a liter of oxygen 1.4292 grams[1] and its molecular weight 32, by dividing the latter by the former. The other basic factor is that in these six gaseous elements the molecules consist of two atoms, that is, they are diatomic.

The application of the constants in Tables I and III to the solution of practical problems is described by typical examples given in Section IV.

---

[1] This value is the one used in the well known Landolt-Boernstein tables as the basis for calculating the densities of gases.

	val.	
Manganese	2	1.0247
Iron	2	1.0416
Nickel	2	1.0946
Cobalt	2	1.1000
Yttrium	3	1.1031
Tin	4	1.1071
Uranium	8	1.1109
Tungsten	6	1.1441
Copper	2	1.1858
Osmium	6	1.1870
Tellurium	4	1.1892
Molybdenum	3	1.1939
Platinum	6	1.2138
Zinc	2	1.2194
Rhodium	3	1.2797
Gallium	2	1.3039
Cerium	4	1.3081
Chlorine	1	1.3229
Tantalum	5	1.3543
Tungsten	5	1.3729
Indium	3	1.4277
Potassium	1	1.4588
Selenium	2	1.4774
Uranium	6	1.4811
Antimony	3	1.4948
Bismuth	5	1.5520
Iodine	3	1.5784
Strontium	2	1.6347
Tungsten	4	1.7162
Lanthanum	3	1.7286
Cerium	3	1.7442
Praseodymium	3	1.7522
Uranium	5	1.7774
Molybdenum	2	1.7908
Neodymium	3	1.7945
Iridium	4	1.8011
Platinum	4	1.8206
Samarium	3	1.8704
Europium	3	1.8903
Lead	4	1.9326
Gadolinium	3	1.9562
Terbium	3	1.9798
Palladium	2	1.9904
Dysprosium	3	2.0209
Holmium	3	2.0333
Erbium	3	2.0855
Thulium	3	2.0955
Cadmium	2	2.0967
Indium	2	2.1415
Ytterbium	3	2.1577
Thorium	4	2.1676
Lutecium	3	2.1763
Tin	2	2.2142
Uranium	4	2.2217
Copper	1	2.3717
Tellurium	2	2.3784
Gold	3	2.4524
Thallium	3	2.5370
Barium	2	2.5625
Bismuth	3	2.5867
Uranium	3	2.9623
Bromine	1	2.9817
Rubidium	1	3.1880
Tungsten	2	3.4323
Platinum	2	3.6413
Mercury	2	3.7420
Lead	2	3.8651
Silver	1	4.0248
Radium	2	4.2158
Iodine	1	4.7351
Caesium	1	4.9549
Gold	1	7.3572
Mercury	1	7.4840
Thallium	1	7.6109

Table III

ELECTROPHYSICAL EQUIVALENTS OF GASES BY VOLUME

The following constants, which are independent of the atomic weights or vapor densities, apply to all the six elements, BROMINE, CHLORINE, FLUORINE, HYDROGEN, NITROGEN, and OXYGEN, which in their free state are normally gases, and all of which are diatomic. They are here assumed to have the properties of a perfect or ideal gas. The constants are for a *unit change of valence,* hence for any other change of valence (for oxygen it is generally 2) the constants of the first group must be multiplied by it and those of the second group divided by it.

The volumes of the gases are for 0° C and 760 mm.

8.6193	coulombs per cubic centimeter;
2.3943	ampere-hours per liter;
67.798	ampere-hours per cubic foot.

The reciprocals are:

0.11602	cubic centimeter per coulomb;
0.41767	liter per ampere-hour:
14.750	cubic feet per 1000 ampere-hours.

Table IV

VALENCES OF THE ELEMENTS IN THEIR COMBINATIONS

Prepared by Prof. Jos. W. Richards

The following are the practical or actual valences irrespective of any interpretation involving structural formulas. There are additional valences which occur more rarely, and still others about which there may be some doubt. By the word "salts" is meant oxides, sulfides, sulfates, chlorides, chlorates, etc.

NAMES	VALENCES
Aluminum	Salts + III; aluminates + III.
Antimony	Antimonous salts + III; antimonic salts + V; antimonites + III; antimonates + V; antimonides – III, sometimes – I and – II.
Argon	Non-valent; forms no known combinations.
Arsenic	Arsenious salts + III; arsenic salts + V; arsenites + III; arsenates + V; arsenides – III, sometimes – I and – II.
Barium	Salts + II; peroxide + IV.
Bismuth	Bismuthous salts + III; bismuthic salts and bismuthates + V.
Boron	Salts + III; borates + III; perborates + V.
Bromine	Bromides – I; hypo-bromites + I; bromites + III; bromates + V; perbromates + VII.
Cadmium	Salts + II.
Caesium	Salts + I.
Calcium	Salts + II.
Carbon	Carbonates + IV; salts usually + IV; in CO + II; hydrocarbons, free valences – I to – IV.
Cerium	Cerous salts + III; ceric salts + IV.
Chlorine	Chlorides – I; hypochlorites + I; chlorites + III; chlorates + V; perchlorates + VII; in chlorine oxides + I, + III, + IV, + V, + VII.

Chromium	Chromous salts + II; chromic salts + III; tri-oxide + VI; chromites + III; chromates or di-chromates + VI.
Cobalt	Cobaltous salts + II; cobaltic salts + III.
Columbium	CbO + II; CbO_2 + IV; columbic salts and columbates + V.
Copper	Cuprous salts + I; cupric salts + II.
Dysprosium	Salts + III.
Erbium	Salts + III.
Europium	Salts + III.
Fluorine	Fluorides – I; all compounds – I.
Gadolinium	Salts + III.
Gallium	Salts + III.
Germanium	Germanous salts + II; germanic salts + IV; germanites + II; germanates + IV.
Glucinum	Salts + II.
Gold	Aurous salts + I; auric salts + III; aurates + III.
Helium	Non-valent; forms no known combinations.
Holmium	Salts + III.
Hydrogen	+ I; in peroxide + II.
Indium	Salts + III.
Iodine	Iodides – I; hypo-iodites + I; iodites + III; iodates + V; per-iodates + VII; iodic oxide + V.
Iridium	Iridous salts + III; iridic salts + IV.
Iron	Ferrous salts + II; ferric salts + III; ferrites + III; ferrates + VI.
Krypton	Non-valent; forms no known combinations.
Lanthanum	Salts + III.
Lead	Usual salts or plumbic salts + II; di-oxide or peroxide and plumbates + IV; sub-oxide + I.
Lithium	Salts + I.
Lutecium	Salts + III.
Magnesium	Salts + II.
Manganese	Manganous salts + II; manganic salts + III; di-oxide or peroxide + IV; manganates + VI; permanganates + VII.
Mercury	Mercurous salts + I; mercuric salts + II.
Molybdenum	Molybdous salts + II; molybdic salts + III; di-oxide + IV; tri-oxide and molybdates + VI.
Neodymium	Salts + III.

Neon	Non-valent; forms no known combinations.
Nickel	Nickelous salts + II; nickelic salts + III.
Niton	Non-valent; forms no known combinations.
Nitrogen	Ammonia and ammonium salts (NH_4 salts) − III; most organic nitrogen compounds − III; nitrous oxide + I; nitric oxide + II; sesqui-oxide and nitrites + III; di-oxide (peroxide) + IV; nitric anhydride and nitrates + V. (In ammonium nitrite and nitrate the N in the NH_4 radical is − III and in the acid radical + III or + V.)
Osmium	Osmous salts + II; osmic salts + IV; sesquioxide + III; tri-oxide and osmates + VI; peroxide and perosmates + VIII.
Oxygen	Oxides, salts, etc. − II.
Palladium	Palladous salts + II; palladic salts + IV.
Phosphorus	Phosphorous salts and phosphites + III; phosphoric salts and phosphates + V; phosphides − III; hypophosphites + I; hypophosphates + IV.
Platinum	Platinous salts and platinites + II; platinic salts and platinates + IV.
Potassium	Salts + I.
Praseodymium	Salts + III.
Radium	Salts + II.
Rhodium	Rhodous salts + II; rhodic salts + III; dioxide + IV.
Rubidium	Salts + I.
Ruthenium	Ruthenous salts + II; ruthenic salts + III; ruthenic anhydride and ruthenates + VI; per-ruthenic anhydride + VIII.
Samarium	Salts + III.
Scandium	Salts + III.
Selenium	Selenites + IV; selenates + VI; selenides − II.
Silicon	Silicides − IV; salts, oxide and silicates + IV.
Silver	Salts + I.
Sodium	Salts + I.
Strontium	Salts + II.
Sulfur	Sulfides − II; di-sulfides − I; SO_2 and sulfites + IV; SO_3 and sulfates + VI; hyposulfites (thio-sulfates) + II; S_2O_3 + III; S_2O_7 and per-sulfates + VII.

Tantalum	Salts and tantalates + V.
Tellurium	Tellurides − II; di-tellurides −I; tellurous salts + II; telluric salts and tellurites + IV; TeO_3 and tellurates + VI.
Terbium	Salts + III.
Thallium	Thallous salts + I; thallic salts + III.
Thorium	Salts + IV.
Thulium	Salts + III.
Tin	Stannous salts and stannites + II; stannic salts and stannates + IV.
Titanium	Titanous salts and titanites + III; titanic salts and titanates + IV.
Tungsten	WO + II; WO_2 and WCl_4 + IV; WCl_5 +V; tungstic oxide and tungstates + VI.
Uranium	Uranous salts + IV; uranic salts and uranates + VI; oxides + III, + IV, + VI, + VIII; chloride + V.
Vanadium	Vanadates + V; vanadous salts + III; VO + II; VO_2 + IV.
Xenon	Non-valent; forms no known combinations.
Ytterbium	Salts + III.
Yttrium	Salts + III.
Zinc	Salts + II.
Zirconium	Salts and zirconates + IV.

Section IV

CALCULATIONS INVOLVING ELECTROCHEMICAL EQUIVALENTS. EXAMPLES

There are in general three ways of making calculations which are based on Faraday's law and therefore involve electrochemical equivalents, that is, calculations of the quantities of the materials by weight which are deposited, dissolved, or otherwise chemically changed when an electric current is passed thru an electrolyte. The simplest cases are so easy to calculate with the aid of the accompanying table that very little and in some cases no knowledge of chemistry is required; even in some of these simplest ones, however, it is essential to know what the so-called "valence" is of the chemical element in the problem; whenever it is unity it can be neglected; those who do not know how to determine it had better consult a chemist; an explanation of the meaning of this term is given in Appendix I. In the more involved cases a knowledge of chemistry is required for making the calculations; some of the elementary principles of chemistry are given in Appendix II.

The first and simplest method of making such calculations is to use the figures given in Table I, which includes all the elements and practically all the valences occurring in practice; all that is necessary then is to multiply the proper figure from the table (being careful about the valence) by the quantity of material or current and the time stated in the particular problem; the table saves the most tedious parts of the complete calculations, as they have already been made in calculating the values given in it; the table is a convenience but not a necessity, as the calculations could all be made without it, tho they are then more laborious and sometimes far more so.

The second method is based on the single electrochemical constant called a "faraday" which is the same for all the elements. It is the electric charge carried by a gram ion when the valence is unity. No table is then required, but the calculations are often quite lengthy, tedious, and confusing. It is then necessary to know the value of the faraday; its best known value at the present time is very nearly 96,500 coulombs or about 26.80 ampere-hours (more accurately 96,493.7 and 26.8038). As before, it must be known what the valence is in the particular problem. For valences 2, 3, 4, etc. (whether positive or negative), the charges are 2, 3, 4, etc. faradays.

When the elements are set free in the form of gases or vapors, and when the amounts are desired in terms of their volumes instead of their weights, there exists a still simpler constant than the faraday, because the amount of electricity required to set free a liter of the vapor of any element is always the same per unit atom in the molecule and per unit change of valence. This constant for 0° and 760 mm. is 4309.7 coulombs or 1.1971 ampere-hours per liter. This need then merely be multiplied by the number of atoms in a molecule of the gas or vapor, called its atomicity (and apparently always a simple whole number), and by the change of valence (also generally a simple whole number) to give the result directly. For the atomicity of an element works on chemistry should be consulted. The change of valence must be determined in each particular case; in all ordinary cases that of hydrogen is 1 and of oxygen 2. For the six gaseous elements, the atomicity of all of which at ordinary temperatures is 2, this constant and its derivations are given in Table III. As the calculations are then so simple and direct no further explanations are necessary (see Example 2 below).

The third general method of making electrochemical calculations is first to make the electrochemical part of it for some other convenient element or radical, like hydrogen, oxygen, zinc, SO_4, or some element in the particular reaction for which the calculation is simple and surely correct, and then by a purely chemical calculation determine what the chemical equivalent of this amount of the intermediary element is in terms of the one for which the figures are desired. When the valences of the two are the same, their chemical equivalent weights are in proportion to their atomic weights; when the valences are different reduce the relative weights to unity valence by dividing the atomic weights by the respective valences. This methods always requires some knowledge of chemistry and sometimes considerable. In some of the more involved, complicated, or obscure cases this is the safest and surest method, as it is less liable to be confusing. It is always more lengthy and tedious than the first method, and sometimes much more so. If hydrogen is always used as this intermediary (because its atomic weight is practically unity) the table is rendered unnecessary except for the values for hydrogen.

With these brief statements about the three methods they are best explained in detail by the following set of examples and the remarks accompanying them. These examples have been chosen to be characteristic of the more usual typical cases and include also a few of the unusual ones.

Example I. *Simplest case. Valence may be neglected.* How much silver will be deposited per hour by 10 amperes? The valence of silver being always unity can be neglected. For silver, column 7 of the table states that one ampere-hour will deposit 4.025 grams, hence 10 amperes will deposit 40.25 grams per hour (one troy ounce is equal to 20 pennyweight or to 31.104 grams).

To calculate this by the second method, without the table, one must know that every gram ion of the silver (or of any other element whose valence is unity) carries a charge of one "faraday" which is equal to about 96,500 (accurately 96,493.7) coulombs of electricity (a coulomb is equal to an ampere flowing for one second). In cases occurring in practice it is often more convenient to use its equivalent 26.8038 ampere-hours. A gram ion of silver is as many grams as are expressed by its atomic weight, hence for silver the weight of a gram ion is 107.88 grams. 10 amperes for one hour are equal to 10×3600 seconds $= 36,000$ coulombs (or ampere-seconds). Dividing this by the faraday, 96,500 coulombs gives 0.373 gram ions, and as a gram ion of silver weighs 107.88 grams, the desired result is $0.373 \times 107.88 = 40.25$ grams, as before. Or the faraday may in this case be more conveniently taken as 26.8 ampere-hours, then 10 ampere-hours divided by 26.8 equals 0.373 gram ions, as before. The use of the table saves these somewhat lengthy computations and the errors arising in multiplying when one should have divided, or the reverse, as the problems are often the reverse of the present one.

In the third method of making this calculation, which may be resorted to by those who are not used to the conception of valences, or in some complicated or involved cases, select some other convenient intermediary element, like hydrogen for instance, for the electrochemical part of the calculation, using the values for that element in the table, and then by a purely chemical calculation determine the chemically equivalent weights of that intermediary element and of the original one; the electrochemical equivalents will then be in the proportion of these weights.

In many cases hydrogen is selected as this intermediary element, chiefly because its atomic weight is practically unity, hence the corresponding weights of all the other elements are equal to their atomic weights which must however be divided by the valence which they have in that particular problem when it is not unity. Another reason for selecting hydrogen is that the whole table is then reduced to the few figures for hydrogen alone. Hence selecting hydrogen in the present problem, find from the table how much hydrogen will be set free in one hour by the 10 amperes; the table gives 0.03761 grams for one ampere, hence multiplying by 10 gives 0.3761 grams.

To find the chemically equivalent weights of silver and hydrogen, it is in this case sufficient (because both have a valence of unity) to use their atomic weights 107.88 and 1.008; for most purposes it is accurate enough to assume that of hydrogen to be unity. The valence of silver and hydrogen are both unity and may therefore here be neglected; if instead of silver it were zinc, for instance, whose valence is always 2, the atomic weight of zinc, 65.37, would have to be divided by this valence 2 to get the chemically equivalent weights, which would then be 32.69 and 1.008.

Having found the chemically equivalent weight of silver to be 107.88 ÷ 1.008 = 107.02 times that of hydrogen, multiply the above 0.3761 grams of hydrogen by 107.02, giving as before 40.25 grams of silver per hour, for 10 amperes.

While this method is a somewhat involved one for such a simple case as the present one, it is explained here because it is often a safe method to resort to (even if only as a check) in the more complicated and involved cases like those in which there is no deposit or merely a change of valence, as is the case for instance with depolarizers, or when the valence is not known or is obscured; and in some of these more involved cases it may be more convenient to use some other element which is actually involved in the particular reaction, instead of hydrogen; these cases will be described below in other examples.

Example 2. *Gas.* How many amperes will it take to generate a cubic foot of hydrogen per hour? A liter of hydrogen at 0°C. and 760 mm. weighs 0.09004 grams, hence a cubic foot will weigh $0.09004 \times 28.32 = 2.55$ grams. The valence of hydrogen, being unity, can be neglected. From Table I, column 8, it takes 26.59 ampere-hours to generate one gram; hence 2.55 grams will require $26.59 \times 2.55 = 67.8$ ampere-hours; therefore it will take 67.8 amperes to generate one cubic foot of hydrogen per hour.

Hydrogen being a gas and as the amount is here required in terms of volume and not of weight, this same result can be obtained directly from Table III.

Example 3. *Anode. Valence* 2. How long will 10 pounds of copper anodes last in a copper plating or electrotyping bath in which the average current is 50 amperes, the solution being a cupric salt, like sulfate of copper? The valence of copper in a cupric salt is 2, hence from the table, column 10, one pound of copper at this valence will be consumed by 382.5 ampere-hours, which at 50 amperes means a little over 76 hours.

In making this calculation by means of the unit faraday, it must be remembered that the copper in this case has a valence of 2, hence each gram ion of 63.57 grams now carries a charge of 2 faradays or 193,000 coulombs. 50 amperes equal 180,000 coulombs per hour, which divided into 193,000 gives 1.072 gram ions of 63.57 grams, making 68.15 grams or 0.150 lbs., hence 10 lbs. will last 76 hours, as before.

In making the calculation by the other method based on hydrogen as an intermediary element it must not be forgotten that the equivalent weight of copper is now the atomic weight divided by 2, because the valence now is 2.

Example 4. *Primary battery.* How many pounds of zinc will be consumed per hour (not including local action) in a battery of primary cells generating 1 kilowatt, the available voltage being 1.7 per cell? Zinc always has the same valence, 2; when the figures in the table are used this valence has already been included in them and therefore the valence may be ignored in the subsequent calculations. For zinc, column 9 gives the constant 2.688 and states that when divided by the volts this is equal to the pounds per kilowatt-hour. Dividing 2.688 by 1.7 gives 1.58 pounds per hour for one kilowatt. The zinc consumption will of course be the same for a single large cell as for a battery of cells, and is independent of whether the cells are connected in series or in parallel.

To calculate this zinc consumption from the unit "faraday," that is, without the table, the valence 2 must be taken into account. This unit is the charge carried by a monovalent gram ion, that is, it is for a valence 1. For any other valence this constant must be multiplied by the valence; hence for zinc it is 96,500 × 2 = 193,000 coulombs. One kilowatt at 1.7 volts means 588 amperes which for one hour is equal to 3600 × 588 = 2,116,800 coulombs; dividing by 2 faradays or 193,000 coulombs, gives 10.96 gram ions of zinc, and as one gram ion is numerically equal to the atomic weight, hence is 65.37 grams, this equals 10.96 × 65.37 = 716.0 grams; multiplying by 0.002205 gives 1.58 pounds, as before. This example again shows how much calculation is saved by using the table.

Single valence. The above examples show how to use the table when the chemical element is set free or dissolved and has only a single valence, in which cases there can be no question as to what the valence is. The table is used in the same way with those elements which have several valences, as stated in column 4; it is then of course of the utmost importance to know which of its valences is the one involved in the particular problem; the importance of this is shown in the next paragraph.

Several valences. When copper, for instance, is deposited from the ordinary copper sulfate, $CuSO_4$ (cupric sulfate), its valence is 2, as the copper then is the chemical equivalent of two atoms of hydrogen in the corresponding hydrogen compound H_2SO_4 (sulfuric acid). Hence with that electrolyte the constants in the table for the valence 2 must be used. If however it is deposited from the cuprous sulfate Cu_2SO_4, the copper is the direct equivalent of the hydrogen, hence its valence then is 1. As will be seen from the table, the same current then deposits twice as much copper, hence the importance of using the constants for the correct valence.

When the table is not used, or only indirectly, the changes necessary in the calculations when the valence is anything else than unity, have already been described above in examples 1, 3, and 4.

Change of valence. The above cases are the more usual ones in which some chemical element like a metal or gas is set free or dissolved at the electrodes. In some other cases however the element is neither set free nor dissolved; in these the current merely changes the valence of the element from one value to another. This is the case for instance in many of the so-called depolarizers of batteries, like in the manganese of the peroxide in the usual dry cell, the lead of the positive plate of the lead storage battery, the chromium or nitrogen of the corresponding acids in the Grove or the Bunsen cells. Also in such reactions as the changing of ferrous into ferric salts, cuprous to cupric salts, etc., or the reverse.

In all such cases the simplest rule is to find out what the valences are before and after the passage of the current, the difference between them will then be the change of valence, and it is this difference which must be used in column 4 of the table to find the corresponding electrochemical equivalents. The function of the current may be said to be the changing of the valence of an element; and for a unit amount of any given element a certain definite amount of electricity is required to change the valence by one unit, no matter whether that valence was high or low; for instance, it takes just as much electricity to reduce a gram of copper from a cupric (valence 2) to a cuprous (valence 1) salt, in which operation the change of valence is 1, as it does to deposit a gram of the metal from the cuprous salt in which the change of valence is also 1; after metals or other elements have been set free as such, their valence is zero, as they are then no longer in combination with other elements and therefore then have no existing bonds; hence depositing a free element is really also a case of change of valence (see Appendix I).

In subtracting one valence from another the difference may have the negative sign, as in subtracting 3 from 2; the sign of this difference need not be considered as it signifies merely the direction of the current but not the amount; hence all the valences in the table apply equally well to the negative as to the positive values. These features of valences are described more fully in Appendix I.

Example 5. *Depolarizer. Change of valence.* How much peroxide of manganese is required as a depolarizer in a dry cell for a discharge of 100 ampere-hours? In this reaction 2 MnO_2 is reduced to Mn_2O_3, the remaining atom of oxygen being that which performs the operation of depolarizing by combining with the ion which would otherwise tend to be set free there and cause polarization.

The valence of the manganese in the original material is 4 (as oxygen here has a valence of 2), while in the resulting product it is 3 (the oxygen now having 6 bonds, each of the two manganese atoms must have 3), hence the difference or change of valence is 1. From the table, column 9 for manganese, valence 1, 4.518 pounds of the element manganese are required for 1000 ampere-hours, hence 0.4518 lb. for 100 ampere-hours. This is for the element manganese; the corresponding amount of the peroxide is then determined as usual by the well known chemical calculations; thus the molecular weight (or more correctly the formula weight) of the peroxide MnO_2 is $54.93 + (16 \times 2) = 86.93$, and that of manganese alone is 54.93; hence 0.4518 lb. of Mn $\times 86.93 \div 54.93 = .715$ or about 3/4 lb. of the peroxide.

The same result may be obtained without involving the change of valences, but it will be found to be far more cumbersome. In that case write out the complete chemical equation of the reaction involving the zinc, the manganese oxides, and the ammonium chloride. Then calculate the amount of zinc consumed by the 100 ampere-hours, as described above, using the constants in the table, and then from the equation by purely chemical calculations, determine the amount of the peroxide corresponding to that amount of zinc.

Subscripts may be ignored. After having determined the valence involved in a reaction, the subscripts in the chemical formulas of compounds can be ignored entirely in these electrochemical calculations. For a given valence of an element an ampere-hour corresponds to a fixed and definite amount of the element and is entirely independent of any arbitrary chemical formula.

Thus from cuprous chloride CuCl the amount of chlorine involved by one ampere-hour is exactly the same as in cupric chloride $CuCl_2$, namely 1.323 grams, altho the subscript is twice as great in the second case; the valence of the chlorine is the same in both, namely 1. For the copper the subscripts are the same in both (unity), yet the amount of copper deposited per ampere from CuCl is twice as great as from $CuCl_2$ because the valence is half as great. The subscripts are important for determining the valences, but beyond that they should be ignored in such calculations, as they may cause confusion. For the indirect method of calculation in which the whole chemical equation must be written out, the subscripts are of course important for balancing the equation and must be considered in the purely chemical part of the calculation.

Coefficients may be ignored. What was said above about subscripts is equally applicable to the coefficients in chemical formulas; they moreover are not even necessary to determine the valence. This is illustrated by the following example.

Example 6. *Ignoring coefficients.* How much nitric acid will be required in a Bunsen cell for 100 ampere-hours, assuming that the nitric acid HNO_3 is all reduced to nitric oxide NO?

The chemical formula for this reaction is

$$3\ Zn + 3\ H_2SO_4 + 2\ HNO_3 = 3\ ZnSO_4 + 2\ NO + 4\ H_2O$$

which it will be seen contains numerous coefficients.

In the simplest and most direct form of calculation based on the change of valence, all that is necessary to know is that the valence of the nitrogen in the nitric acid is 5 and in the nitric oxide it is 2, hence the change of valence is 3; all these coefficients may therefore be neglected, and in fact need not even be known. From the table the constant for nitrogen for a change of valence of 3 is 0.3841 pounds per 1000 ampere-hours; for 100 ampere-hours it is therefore 0.0384 lb. From this the amount of the acid is calculated by the usual chemical method; thus the atomic weight of N = 14.01, and the molecular weight of $HNO_3 = 1.008 + 14.01 + 48. = 63.02$; therefore 0.0384 lb. $\times 63.02 \div 14.01 = .173$ lb. of nitric acid;

this of course refers only to the nitric acid itself and does not include the water in which the commercial acid is dissolved.

If however the calculation is made in the longer indirect way, that is, by first determining electrochemically the amount of zinc corresponding to the 100 ampere-hours, and then chemically the amount of nitric acid corresponding to this amount of zinc, — the coefficients of course enter into the calculation, tho only in the purely chemical part of it. Thus from the table 100 ampere-hours corresponds to .269 lb. of zinc, no matter what the coefficient of the zinc is in this formula. From the equation 3 Zn corresponds to 2 HNO_3, hence the amounts of zinc and nitric acid are in the proportion of the weights of these two quantities. The atomic weight of zinc is 65.37 and the molecular weight (or formula weight) of nitric acid is 63.02 (see above); hence .269 lb. × (2 × 63.2) ÷ (3 × 65.37) = .173 lb. of nitric acid, as before.

Intermediate reactions may be ignored. The reaction in example 6 involves an intermediate reaction also; the zinc is dissolved in the sulfuric acid in which it replaces the hydrogen, and this hydrogen then reduces the nitric acid; this at least may serve as a simple explanation of the reaction. In the direct method of calculation based on the change of valence all such intermediate reactions may be ignored, while in the chemical part of the indirect method they may sometimes have to be known in order to write out the chemical equation. The amount of nitrogen oxidized or reduced by one ampere-hour, involving a given change of its valence, is a fixed and definite quantity, and is entirely independent of any other reactions which may be occurring at the same time, except of course if they are resultant reactions of a purely chemical kind, often termed secondary reactions.

Involved reactions. The above examples illustrate the simplest kinds of cases involving calculations of electrochemical equivalents. The following examples will serve to illustrate some of the less simple cases which involve features that are different from those in the more usual ones and which might sometimes give rise to confusion.

Example 7. Nothing set free or dissolved at one of the electrodes. If the cathode is in copper sulfate and the platinum anode is in ferrous sulfate, copper will be deposited on the cathode as usual; but at the platinum anode the corresponding SO_4 ion will not set free oxygen as is more usual, but will oxidize the ferrous sulfate into the ferric, hence nothing will be set free or dissolved there. The iron solution acts as a depolarizer at the anode by combining with the SO_4, thereby preventing it from forming a film of oxygen gas over the anode.

However the somewhat unusual fact that nothing is set free or dissolved at the anode involves no difficulties in the electrochemical calculation for that electrode when based on the change of valence, and need lead to no confusion. The iron salt has been changed at that electrode from ferrous to ferric, which is a true electrochemical reaction; it means that its valence has been changed from 2 to 3, hence by 1 unit; the amount of iron so changed per ampere-hour is therefore found directly from the table, column 7, for valence 1, namely 2.083 grams per ampere-hour. The amounts of the sulfates corresponding to this amount of the iron, are then readily determined from the purely chemical calculations.

The equation of this reaction is

$$CuSO_4 + 2\ FeSO_4 = Cu + Fe_2\ (SO_4)_3$$

The valence of the radical SO_4 is 2, as it combines with 2 hydrogen atoms in H_2SO_4; from its valence the valences of the iron in these ferrous and ferric salts are evident from their formulas, 2 in the first and $(3 \times 2) \div 2 = 3$ in the second.

The amount of iron salts could be determined also without considering the valences by finding first how much copper will be deposited by a given current and then by a purely chemical calculation, using the above equation, determine the corresponding amounts of the iron salts.

Example 8. *Nothing set free or dissolved at either electrode.* If a platinum cathode is in a solution of ferric sulfate, and a platinum anode is in a solution of ferrous sulfate (the latter like in example 7), then at the cathode the ferric sulfate will be reduced to the ferrous, while at the anode the ferrous will be oxidized or adduced to the ferric; hence nothing will be set free or dissolved at either electrode. The SO_4 ions will go from the cathode to the anode.

The reaction is

$$Fe_2(SO_4)_3\ \text{(at cathode)} + 2\ FeSO_4\ \text{(at anode)} =$$
$$2\ FeSO_4\ \text{(at cathode)} + Fe_2(SO_4)_3\ \text{(at anode)}.$$

The valence of the iron in the ferric state is 3 and in the ferrous 2, hence there is a change of 1, and this change is the same in amount at each electrode, tho of opposite sign, which merely signifies the relatively reverse direction of the current. The electrochemical equivalent is therefore found directly from the table to be 2.083 grams of iron per ampere-hour; this applies to either electrode.

This is a case in which the method of calculation based on the change of valence is far simpler than with the older methods, as there is now nothing tangible set free or dissolved at either electrode which could be used as a basis, as was the case in all of the other examples. The iron cannot now be used as a basis because it is not deposited and has a different valence at each electrode; to use either of these valences would give a totally wrong result.

A possible way of making this calculation without considering the change of valence, would be to use the radical SO_4 as a basis, as this is in effect transferred from one electrode to the other just as the metal is in electroplating, and its valence is the same, namely 2, in both of the salts, hence can be neglected; having the same valence its electrochemical equivalent at each electrode is the same per ampere-hour.

Its electrochemical equivalent is not given in the table because it is not an element, but it can readily be determined from any of the sulfates, such as $FeSO_4$. Thus the iron in this sulfate has a valence of 2, hence its electrochemical equivalent from the table is 1.042 grams per ampere-hour. As every atom of iron corresponds to one molecule of SO_4 the amount of the latter in grams per ampere-hours will be in the proportion of their atomic weights. That of iron is 55.84 and that of SO_4 is $32.06 + (16 \times 4) = 96.06$. Hence 1.042 grams $\times\ 96.06 \div 55.84 = 1.79$ grams of SO_4 per ampere-hour.

At the anode one SO_4 combines with two $FeSO_4$ to form one $Fe_2(SO_4)_3$; hence 2 Fe (atomic weight $2 \times 55.84 = 111.68$) corresponds to one of SO_4 (atomic weight 96.06). As there are 1.79 grams of SO_4 per ampere-hour, there will be $1.79 \times 111.68 \div 96.1 =$

2.083 grams of iron involved at each electrode per ampere-hour, the same as was found above by a far simpler calculation. A similar calculation made for the cathode reaction will give the same result except that what is a gain of SO_4 at one is a loss at the other.

It will be noticed that the end results are chemically the same as those at the start, hence nothing has been accomplished other than changing the positions of the two solutions, which should be separated by a porous cup. It is analogous to electroplating in which the end results are also chemically the same, the metal being merely transferred from the anode to the cathode.

It is assumed of course that this reaction is not carried out faster than the solutions in contact with the electrodes can be replaced by diffusion, otherwise some other reactions will take place, like the deposition of iron or the evolution of oxygen. As this reaction involves no resultant chemical change it should require no more voltage than that necessary to overcome the resistance; hence using a voltage too low to set free iron or oxygen, ought to prevent these other reactions from taking place.

Example 9. The same as Example 8 but involving in addition a purely chemical reaction. The platinum anode is again in a solution of ferrous sulfate, but the cathode now is in a solution of chromic and sulfuric acid. Again nothing will be set free or dissolved at either electrode. The complete equation is

$$2\ H_2CrO_4 + 6\ H_2SO_4 + 6\ FeSO_4 = \\ Cr_2(SO_4)_3 + 8\ H_2O + 3\ Fe_2(SO_4)_3$$

The chromic acid will be reduced at the cathode which would form a precipitate but this is dissolved in the sulfuric acid forming chromium sulfate. The chromium at the cathode has changed its valence from 6 to 3, hence the difference is 3; its amount can therefore be found directly from the table. At the anode the change of valence of the iron is 1, namely from 2 in the ferrous to 3 in the ferric state; hence its amount can also be found directly from the table.

The sulfuric acid however has a double function, half of it being electrolyzed to give the SO_4 to the ferrous sulfate at the anode, the hydrogen from it going to form water, while the other half acts purely chemically to dissolve the reduced chromic acid, forming chromium sulfate and water. The latter half must therefore not be included in the electrochemical calculations, but must be added to that required electrochemically in order to get the total acid for the complete reaction. In such complicated reactions it is safest to use the chromium or the iron in the electrochemical calculations and then calculate the amount of sulfuric acid by purely chemical means from the above equation.

The metals in solution at the anode and cathode being different (iron and chromium), the calculations might again be made as suggested in the previous example 8, by using SO_4 as a basis, as it is this that may be said to be what is transferred from one electrode to the other.

It may be of interest to note here that this reaction forms an odd kind of storage battery, in which only the two liquids enter into the reaction and carry the energy, the plates themselves remaining completely unchanged. The fresh liquids could be supplied to the battery as the source of the energy, and the exhausted liquids only (and not the whole battery) would be taken to a power station and recharged by means of a current. One of the objections to it is that it is a two fluid battery, hence requires porous partitions to keep the liquids separated, and that they will nevertheless gradually contaminate each other.

Example 10. *Nothing is set free or dissolved at one of the electrodes, and the current appears to do double duty on the same electrolyte.* If the electrodes are both platinum and there is only a single solution of cuprous chloride, CuCl, copper will be deposited at the cathode with a valence of 1, while at the anode the chlorine will raise (oxidize, or better, adduce) the cuprous to cupric chloride, $CuCl_2$, hence nothing will be set free or dissolved at the anode. The chemical equation is

$$2\,CuCl = Cu + CuCl_2$$

The amount of copper deposited per ampere-hour is readily calculated from the table, remembering that the valence now is 1 and not 2 as is more usual; that is, there will be twice as much deposited per ampere-hour as from the more usual copper solutions. But the facts that nothing is set free or dissolved at the anode and that the amount of cuprous chloride which is changed to cupric is double that corresponding to the copper deposited, may give rise to some confusion.

The chlorine which had been combined with the copper which is deposited on the cathode, tends to be set free at the anode, but it there combines with some of the cuprous chloride, CuCl, to form the cupric, $CuCl_2$. The fact that one molecule of the cuprous chloride is completely decomposed at the cathode, while at the same time another molecule of it is raised to the cupric salt at the anode by the same current, explains why twice as much of the original solution is changed when compared with that which corresponds to the amount of deposited copper. The above chemical equation also shows that in this reaction one part of metallic, free copper corresponds to two parts of the original solution.

To have calculated the amount of cuprous salt which has been acted upon per ampere-hour, from the amount of chlorine arriving at the anode, or from the amount of copper deposited, would have led to entirely wrong results; it is necessary in such cases to consider the actions at both electrodes, and in this particular case the current does a double duty, as the same current changes two molecules of the same compound, one at each electrode. Removing some of the copper (chemically) from cuprous chloride or adding some chlorine to it (chemically) both produce the same effect, namely changing some of it to the cupric chloride; hence in that sense it might be said that the chemical changes of the solution are in this case alike at both electrodes.

Example 11. *Exhaustion of the same electrolyte at both electrodes.* How many ampere-hours will it require to extract all of the lead from a solution of nitrate of lead $Pb(NO_3)_2$ containing 100 grams of lead, when electrolyzed between two platinum electrodes? In this case the lead will be deposited from the solution at both electrodes, it being reduced at the cathode where it be will deposited as metallic lead, and it will be oxidized or adduced at the anode where it will be deposited as peroxide of lead. The residual solution will be nitric acid, and it is here assumed that this will not redissolve the lead on the cathode by local action.

The equation is

$$2\,Pb(NO_3)_2 + H_2O = Pb + 4\,HNO_3 + PbO_2$$

The valence of the lead in the nitrate is 2, in the peroxide it is 4, and in the form of metallic lead it is 0. Hence the change of valence at each electrode is 2; being the same at both, the amount of lead deposited on each electrode will be the same, hence 50 grams. From the table 1 gram at valence 2 will require 0.2587 ampere-hours, hence 50 grams at each electrode will require $50 \times .2587 = 12.94$ ampere-hours.

Or it may be calculated without involving the changes of valence by finding the lead deposited as such at the cathode and then by purely chemical calculations finding the corresponding amount at the anode; the equation shows these two to be the same.

Example 12. *Change of valence involving different signs. Negative Valences.* How much sulfur would be involved per ampere-hour in the oxidation or adduction of hydrogen sulfide, H_2S, into sulfuric acid, H_2SO_4, if it were done electrolytically? The equation is

$$H_2S + 4\ H_2O = 4\ H_2 + H_2SO_4$$

In all the previous examples illustrating the more usual cases involving a change of valence, the two valences of the elements had the same sign before and after the electrolysis, and their signs need therefore not be considered. But in some cases like the present, the sign of the valence changes and therefore becomes very important.

In every compound the bonds representing the valences must always add up to zero. Those of hydrogen are always + and those of oxygen nearly always –. In H_2S the sulfur must therefore have two negative bonds, hence a valence of – 2 to balance the two positive bonds of the H_2. But in H_2SO_4 the sulfur has 6 positive bonds (the oxygen having 8 negative ones, two of which combine with the hydrogen), hence has a valence of + 6.

The change of valence being the *algebraic* difference is therefore in this reaction equal to the difference between − 2 and + 6 which is 8 (the sign of this difference is no longer of importance as it merely refers to the direction of the current). In the table the highest valence given is 6; the figure for valence 1 is 1.196 grams per ampere-hour, hence for a valence of 8 it will be one-eighth of this, namely 0.150 grams of sulfur, as the same current now has to neutralize 8 times as many bonds per gram. This is a very small amount of sulfur for that amount of electricity, hence this reaction would take much current or a long time. This example is described as a simple hypothetical case to show how to make the calculations when there is a change of sign of the valence; as the sulfur would have to pass thru the state of zero valence which means that it is then in its free state, some free sulfur is likely to form in the solution. In practice it is simpler to burn the H_2S in the air to a low oxide and then oxidize a solution of this to a higher oxide by electrolysis.

This calculation could be made also without considering this change of valence, by determining from the table the amount of hydrogen liberated per ampere-hour (disregarding the coefficient and subscript) and then by a purely chemical calculation (in which the coefficients and subscripts must be considered) find the corresponding amount of sulfur from the above equation. Thus, from the table, 0.03761 gram of hydrogen is liberated per ampere-hour. From the second half of the equation, for every 8 atoms of hydrogen liberated there will be one of sulfur; from their atomic weights the respective weights will therefore be as 8 × 1.008 is to 32.06. Hence 0.03761 gram of hydrogen per ampere-hour in this case corresponds to 0.03761 × 32.06 ÷ 8.064 = 0.150 grams of sulfur per ampere-hour, the same as before.

Example 13. *A similar case.* When nitric acid is reduced to ammonia there is a similar change of sign of the valence, but in this case it is a change from + to − as it is a reduction, while in the previous case it was a change from − to +, as it was an adduction or a so-called oxidation. The valence of the nitrogen in the acid HNO_3 is + 5 (+ 1 + 5 − 6 = 0), and in the ammonia NH_3 it is − 3 (− 3 + 3 = 0), hence the change is their algebraic difference, 8.

The calculation may be made without involving these valences by starting with the amount of oxygen which would have to be set free, and then determining the nitric acid involved by a purely chemical calculation. In these indirect calculations the element which is set free, as distinguished from merely being changed, is always a good basis for starting such calculations, as was also shown in other Examples.

Example 14. *Partial change of valence.* How much nitric acid is required per ampere-hour when used as a depolarizer in a Bunsen cell, assuming the nitric acid to be changed into ammonium nitrate? The equation is

$$4\,Zn + 4\,H_2SO_4 + 2\,HNO_3 =$$
$$4\,ZnSO_4 + NH_4NO_3 + 3\,H_2O$$

In the nitric acid the valence of the nitrogen is + 5 (+ 1 + 5 − 6 = 0), and in the first part (NH_4) of the ammonium nitrate, it is − 3 (− 3 + 4 + 5 − 6 = 0), hence the change of valence is 8. But part of the nitrogen of the original nitric acid does not change its valence, remaining as NO_3; this part is therefore not involved in the electrochemical part of the reaction. The original acid does a double duty; the equation shows that half of the nitrogen is electrochemically converted into ammonia and the other half remains as NO_3. The former is calculated electrochemically for a change of valence of 8, which is then doubled to get the total.

This may also be calculated by the indirect method without involving these changes of valence. The zinc may then be used as the basis for the electrochemical part of the calculation, the corresponding nitric acid being then determined from it by a purely chemical calculation. In such rare and involved cases as this one the indirect method, tho longer, will no doubt be the safest one to use by those not accustomed to the more convenient conception of changes of valences and negative valences.

PART II

Section V

ELECTROLYSIS

Theory of Electrolytic Dissociation, Faraday's Law, Coulometers

Introductory. Conductors of electricity may be divided into two classes as follows: (1) conductors of the first class which experience a rise of temperature due to the passage of the electric current but do not undergo any chemical change and, (2) conductors of the second class, in which the passage of the electric current is invariably accompanied by chemical decomposition. To the first class belong the metals and their alloys and a few non-metallic elements such as carbon. To the conductors of the second class, termed *electrolytes,* belong solutions of acids bases, and salts, either fused or in solution. Electrolytes are always necessarily compounds and never simple elements. Mercury, for example, is a liquid conductor but it is not electrolyzable. While under ordinary conditions pure water is a non-conductor, it is interesting to note that it becomes a good conductor of electricity when an acid, a base, or a salt is dissolved in it. Although salts are non-conductors at ordinary temperatures, they conduct readily, with simultaneous decomposition, when heated above their melting points. Fused salts form practically the only exception to the rule that pure chemical compounds are non-conductors of electricity. Practically all organic compounds, with the exception of organic acids, bases, and salts, when dissolved in water are non-conductors. Such non-conducting substances, among which alcohol, ether, starch, and sugar may be mentioned as typical examples, are called *non-electrolytes.* It should be borne in mind that the property of electrical conductance is not confined to aqueous solutions alone. The decomposition of an electrolyte resulting from the passage of an electric current thru its solution is known as *electrolysis.*

To Faraday we owe, not only our knowledge of the fundamental law of electrolysis, but also the precise definition of certain terms used in connection with electrolytic phenomena. In his "Experimental Researches"[1] we find the following definitions: "In place of the term pole, I propose using that of *electrode,* and I mean thereby that substance, or rather surface, whether of air, water, metal, or any other body, which bounds the extent of the decomposing matter in the direction of the electric current. The surfaces at which, according to common phraseology, the electric current enters and leaves a decomposing body, are most important places of action, and require to be distinguished apart from the poles, with which they are mostly, and the electrodes, with which they are always, in contact.

. . . The *anode* is therefore that surface at which the electric current . . . enters: . . . it is where oxygen, chlorine, acids, etc., are evolved. . . . The *cathode* is that surface at which the current leaves the decomposing body, . . . the combustible bodies, metals, alkalies, and bases are evolved there. . . . Finally I require a term to express those bodies which can pass to the electrodes, or, as they are usually called, the poles. . . . I propose to distinguish such bodies by calling those *anions* which go to the anode of the decomposing body; and those passing to the cathode, *cations;* and when I have occasion to speak of these together, I shall call them *ions.* Thus, the chloride of lead is an *electrolyte,* and when *electrolysed* evolves the two *ions* chlorine and lead, the former being an *anion,* and the latter a *cation.*"

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[1] "Experimental Researches in Electricity," by Michael Faraday. Everyman's Library, Vol. 576, pp. 112–114.

The different parts of an electrolytic cell are shown in the accompanying diagram, (Fig. 1). It is important to note that, contrary to common usage, it is the surfaces of the plates rather than the plates themselves, which constitute the electrodes of the cell. In batteries the cathode is generally called the positive pole because the current enters the outside circuit from this pole; and the anode (usually zinc) is then called the negative pole. This is reversed in electrolytic baths. Hence the terms positive and negative poles are ambiguous, while the terms anode and cathode are not. The cations move with the current through the electrolytic cell toward the cathode or negative plate and are positively charged, while the anions migrate in the reverse direction toward the anode or positive plate and are negatively charged. In practice it is a matter of great importance to recognize that electrolytic changes occur only in the molecular layer next to the electrodes. Thus, in the electrolysis of a solution of

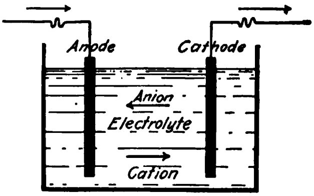

Fig. 1. — Cross-section of an electrolytic cell showing parts.

copper sulfate, when the thin layer of solution next the cathode is exhausted of copper, hydrogen will be evolved, unless the solution is vigorously stirred or the cathode is rotated.

Electrolytic Phenomena. The products obtained at the two electrodes of an electrolytic cell are always different and may be collected in various ways depending upon their nature. When gases are formed they may be collected in appropriate tubes. When insoluble solids are formed they generally adhere to the electrode surface or fall to the bottom of the cell as a precipitate. When soluble substances are produced it is customary to surround one of the electrodes with a porous cup, or to interpose some sort of porous diaphragm between the electrodes, which will minimize the diffusion of the product of electrolysis from the vicinity of the electrode at which it is formed. When a current of electricity is passed between two platinum plates immersed in a solution of silver nitrate, metallic silver is deposited at the cathode while oxygen together with nitric acid is set free at the anode. The two ions, $A\dot{g}$ and NO'_3, are discharged at the cathode and anode respectively: the NO_3 radical is then assumed to react with the water to produce nitric acid and oxygen as indicated by the equation

$$2\,NO_3 + H_2O = 2\,HNO_3 + O$$

The interaction of the NO_3 ion and the water in which the electrolyte was dissolved is known as *secondary action.*[1]

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[1] While the above explanation of secondary action is not in accord with the generally accepted theory of LeBlanc, Zeit. Phys. Chem. 11, 805 (1893), based on the primary decomposition of water, for all practical purposes it may be assumed to be correct.

When a current of electricity is passed between platinum plates immersed in a solution of potassium nitrate, hydrogen is liberated at the cathode and oxygen at the anode. An examination of the solution in the neighborhood of the electrodes reveals the presence of potassium hydroxide at the cathode and nitric acid at the anode. In this case the two ions, $\dot{K}$ and NO'_3, are discharged at their respective electrodes and then a secondary reaction may be assumed to take place between each discharged ion and the water, as shown by the following equations

$$K + H_2O = KOH + H \quad \text{(reaction at cathode}^1\text{)}$$
$$2\,NO_3 + H_2O = 2\,HNO_3 + O \quad \text{(reaction at anode}^1\text{)}$$

If, in this experiment, the negative terminal of platinum is replaced by a cup of mercury, a portion of the potassium will be dissolved, forming an amalgam, thus confirming the primary separation of metallic potassium at the cathode. The reactions taking place at the electrodes during electrolysis are opposite in character; *oxidation invariably occurs at the anode while reduction invariably occurs at the cathode.* These facts are of extreme practical importance and are often either overlooked or are insufficiently emphasized in introductory textbooks of electrochemistry. The anode and cathode reactions accompanying the electrolysis of potassium nitrate, as given above, may be cited as illustrations of this generalization.

Theory of Electrolytic Dissociation. When an electrolyte is dissolved in water, all of the properties of the solution indicate that a larger number of dissolved units are present than in a solution of a non-elec-

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[1] More properly these equations should be written ionically, thus;

$$K + H.OH = \dot{K} + OH' + H$$
$$2\,NO_3 + H.OH = 2\,\dot{H} + 2\,NO'_3 + O$$

trolyte of the same concentration. Since electrolytes are believed to conduct the electric current by virtue of particles, called ions, formed from the molecules of the electrolyte, it is assumed that these ions together with the undissociated molecules are responsible for the abnormal behavior of electrolytic solutions. This hypothesis, put forward by Arrhenius in 1887, is known as the *theory of electrolytic dissociation.* The fundamental assumptions involved in this theory are as follows:

(a) When the molecules of an electrolyte are dissolved in water some of them undergo dissociation into ions. Thus, potassium chloride (KCl) dissociates into the ions $\dot{K}$ and Cl'.

(b) The extent to which the molecules dissociate is dependent upon the dilution of the solution; the more dilute the solution, the greater is the degree of dissociation.

(c) Each ion is highly charged with electricity. It is this electrical charge which differentiates an ion from the corresponding atom, the usual chemical properties of an element being greatly modified by the presence of an electrical charge. Thus, atomic potassium reacts violently with water to form hydrogen and potassium hydroxide, whereas ionic potassium is wholly without action on water.

(d) The ions resulting from the dissociation of an electrolyte are of two kinds. One kind of ion carries a positive charge, and the other carries a negative charge. Since the solution, as a whole, is electrically neutral, it follows that the sum of the positive and negative charges must be equal. The character of the charge carried by an ion may be indicated by writing the usual plus or minus signs over the symbols of the ions or preferably by the use of a dot (˙) for a positive charge and of a dash (′) for a negative charge.

Thus, the electrolytic dissociation of potassium chloride into positively charged potassium and negatively charged chlorine ions may be represented by the equation

$$\mathrm{KCl} = \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Cl}}$$

or

$$\mathrm{KCl} = \dot{\mathrm{K}} + \mathrm{Cl}'$$

Molecules which undergo dissociation into two ions are known as binary electrolytes, while those which yield on dissociation three or four ions are called ternary or quaternary electrolytes respectively. The following equations are examples of the dissociation of ternary and quaternary electrolytes

$$\begin{aligned} \mathrm{K_2SO_4} &= 2\,\dot{\mathrm{K}} + \mathrm{SO}''_4, \\ \mathrm{BaCl_2} &= \overset{\cdot\cdot}{\mathrm{Ba}} + 2\,\mathrm{Cl}', \\ \mathrm{AlCl_3} &= \overset{\cdot\cdot\cdot}{\mathrm{Al}} + 3\,\mathrm{Cl}'. \end{aligned}$$

(e) The properties of a solution of an electrolyte are dependent upon both the ions and the undissociated molecules. The ions are in general more active chemically than the molecules from which they are derived and consequently the influence of the ions is predominant in determining the properties of a solution of an electrolyte.

The theory of electrolytic dissociation, while not free from defects, has proven to be a generalization of great value in the development of the science of electrochemistry. All of the changes which occur during electrolysis can be satisfactorily explained by means of this theory.[1]

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[1] The reader who desires further information concerning the theory of electrolytic dissociation is referred to the following books where a clear exposition of the theory together with some of its applications will be found:

"Theory of Electrolytic Dissociation" — Jones (Macmillan Co.); "The Theory of Electrolytic Dissociation" — Talbot and Blanchard (Macmillan Co.).

"The Nature of Solution"—Jones (D. Van Nostrand Co.).

Migration of the Ions. That electrolysis is not a local phenomenon taking place in the immediate neighborhood of the electrodes, but involves an actual migration of the ions of the electrolyte, may be shown by a variety of experiments of which the following is one of the most striking. The lower part of the U-tube shown in Fig. 2 is charged with a dilute solution of copper sulfate containing about 5 per cent of agar agar and is then allowed to stand until the solution has set to a jelly. Dilute solutions of copper sulfate may be shown to be completely dissociated into ions as indicated by the equation

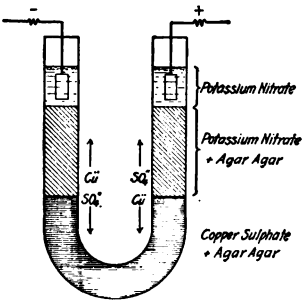

Fig. 2.—Diagram of an experiment to illustrate migration of ions.

$$CuSO_4 = \ddot{C}u + SO''_4$$

Since pure, anhydrous copper sulfate is known to be colorless, and since sodium sulfate, potassium sulfate, and sulfuric acid, all of which substances contain the SO''_4 ion, are colorless, it follows that the blue color of a dilute solution of copper sulfate must be ascribed to the $\ddot{C}u$ ion alone. This conclusion is confirmed by the fact that dilute solutions of all cupric salts have the same color.

When the solution in the U-tube has solidified, the position of the surface of the jelly in each arm of the U-tube is marked by means of strips of gummed paper pasted on the outside of the tube. Then some colorless electrolyte, such as a solution of potassium nitrate to which agar agar has been added, is introduced into each arm of the U-tube. After the agar

agar has set to a jelly, a few cubic centimeters of the potassium nitrate solution containing no agar agar is added to each arm of the tube and two platinum plates introduced as shown in the diagram. The tube is now immersed in ice-water to prevent the softening of the jelly by the heat developed by the passage of the electric current. On applying a current of 110 volts with a 16 candle-power lamp included in the circuit, the blue solution which owes its color to the presence of $\ddot{\mathrm{Cu}}$ ions will be seen to move toward the cathode, ascending on the left-hand side and descending on the right-hand side of the U-tube. While solutions containing $\mathrm{SO''_4}$ ions are colorless, it is reasonable to infer that these ions migrate in the opposite direction. In fact the experiment may be so modified as to reveal the actual movement of the $\mathrm{SO''_4}$ ions toward the anode. The agar agar which is added to prevent the transference of water with the current, has been shown to increase the resistance of the solution relatively little.

By slight modifications of the above experiment, the actual speeds of the ions under a definite potential gradient have been accurately determined. The accompanying table gives the speeds of some of the more common ions in centimeters per second when measured in dilute aqueous solution at 18°C. under a potential difference of 1 volt between plates 1 centimeter apart.

Cations	*Speed, cm./sec.*	*Anions*	*Speed, cm./sec.*
$\dot{\mathrm{H}}$	0.003294	$\mathrm{OH'}$	0.001802
$\dot{\mathrm{Li}}$	0.000346	$\mathrm{Cl'}$	0.000677
$\dot{\mathrm{Na}}$	0.000450	$\mathrm{NO'_3}$	0.000640
$\dot{\mathrm{K}}$	0.000669	$\mathrm{ClO'_3}$	0.000570
$\mathrm{N\dot{H}_4}$	0.000667		
$\dot{\mathrm{Ag}}$	0.000559		
$\ddot{\mathrm{Cu}}$	0.000444		

It will be observed that the two fastest moving ions are the $\dot{H}$ ion and the OH' ion, the former having a speed nearly twice that of the latter.

It has been shown that the speeds of the ions are specific properties, being uninfluenced by the presence of other ions in the same solution. It has also been shown that an increase in the difference of potential between the plates of an electrolytic cell causes proportional increase in the speed with which the ions move. Notwithstanding the fact that the ions move so slowly under a fall of potential of 1 volt per centimeter, it may be shown that enormous forces are involved in imparting to the ions speeds of the order of magnitude of those given in the above table. It has been calculated, for example, that a force equal to a weight of 299,000,000 kilograms is necessary to impart to the $\dot{H}$ ion a speed of 0.003294 cm. per sec. at 18°C. The magnitude of this force is to be ascribed to the extremely small mass and the relatively large surface of the $\dot{H}$ ion.

Faraday's Law. The quantitative relation between the amount of electricity passing thru a solution of an electrolyte and the resulting chemical action was discovered by Faraday about 1835. In his experiments Faraday varied the size and nature of the electrode surfaces, the concentration of the electrolyte, and the amount of current passing thru the solutions in a given time. In all cases he found that the same current produced the same amount of chemical decomposition, or in other words, *for the same electrolyte the amount of chemical decomposition is directly proportional to the amount of electricity which is passed thru the solution of the electrolyte.* When solutions of different electrolytes were subjected to the action of the same current by placing them in series in the circuit, Faraday found that *the masses of the products of electrolysis were directly proportional to their chemical equivalents.* By the term "chemical equivalent" is meant the ratio of the formula-weight of a substance to its valence. Thus, the formula weight of silver is 107.88 and its valence is 1, hence its chemical equivalent is 107.88; similarly, the formula-weight of the SO''_4 ion is 96.06 and its valence is 2, therefore its chemical equivalent is 48.03.

The foregoing statements of the results of Faraday's experiments may be combined in a single generalization as follows: *When the same quantity of electricity is passed thru one or more solutions of the same or different electrolytes, the masses of the substances which separate at the electrodes are directly proportional to their chemical equivalents, and are independent of the concentration and temperature of the solutions, the extent of the electrode surfaces, and all other circumstances.* This generalization is known as *Faraday's Law* and may be regarded as the fundamental law of electrochemical science.

The meaning of the law may be illustrated by the following experiment: If solutions of hydrochloric acid (HCl), sulfuric acid (H_2SO_4), potassium chloride (KCl), cupric sulfate ($CuSO_4$), auric chloride ($AuCl_3$), ferrous chloride ($FeCl_2$), and ferric chloride ($FeCl_3$) are placed in different cells, as shown in Fig. 3, and are then subjected to the action of the same quantity

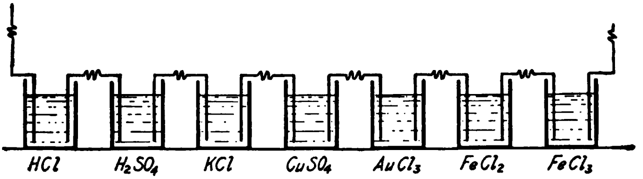

Fig. 3.—Diagram of an experiment illustrating Faraday's law.

of electricity by connecting them in series with a battery of storage cells, it will be found that when 1.008 grams of hydrogen is liberated from each of the two acids. 35.45 grams of chlorine will be set free from each of the chloride solutions, 96.06/2 = 48.03 grams of SO_4 will be set free from the sulfuric acid and cupric sulfate, while the amounts of the metals deposited at the cathode surfaces of the respective cells will be 39.10 grams of potassium, 63.57/2 = 31.7 grams of copper, 197.2/3 = 65.7 grams of gold, 55.84/2 = 27.92 grams of ferrous iron, and 55.84/3 = 18.61 grams of ferric iron.

The foregoing experiment illustrates the fact that the quantity of substance set free by a given quantity of electricity increases inversely as its valence in the solution employed; thus, 27.92 grams of ferrous iron is liberated by the same current which deposits 18.61 grams of ferric iron. This point is of importance in connection with the economic use of electricity in all electrolytic processes. The validity of Faraday's law has been tested by numerous experiments carried out with the utmost care. It has been found to hold, not only for all solvents, but also for fused electrolytes as well.

The Electrochemical Constant. Since the same quantity of electricity — positive or negative — is always carried by a univalent ion, this quantity may be considered as the unit of ionic charge. A bivalent ion will thus carry two unit charges and an n-valent ion will carry n unit charges. In other words, we may think of valence as representing the number of unit charges of electricity which are associated with the respective ions. According to this view Faraday's law may be stated as follows: *Chemically equivalent masses of matter possess the same capacity for electricity.*

The precise measurement of this fundamental quantity of electricity is obviously a matter of great scientific and practical importance. It can be determined by passing a known quantity of electricity thru a solution of an electrolyte and weighing the metal deposited at the cathode surface or measuring the volume of gas set free.

The most satisfactory results have been obtained when a neutral solution of silver nitrate is used, containing about 15 parts of the salt to 100 parts of water, and with a current density of about 0.01 ampere per square centimeter. The silver is deposited on a platinum dish the inner surface of which serves as the cathode, while a silver plate, wrapped in filter paper to retain any particles of silver which may be detached by the current, constitutes the anode surface.

The unit of quantity of electricity is the *coulomb.* This may be defined as the quantity of electricity which has passed through a circuit when a current of 1 ampere has been flowing constantly for 1 second. The mass of a substance in grams deposited by 1 coulomb of electricity is commonly called the *electrochemical equivalent,* of the substance.

The accepted value of the electrochemical equivalent of silver is 0.00111800 gram per coulomb. It is evident, therefore, that 107.88 ÷ 0.00111800 = 96493.7 coulombs of electricity will be required to deposit the equivalent weight of silver in grams.

Since electrochemical equivalents are proportional to chemical equivalents (Faraday's law), it is evident that *96493.7 coulombs of electricity will be required to liberate the equivalent weight of any ion.* This number, 96493.7 coulombs, represents the fundamental electrochemical unit, and is called the *electrochemical constant* or the *faraday.*

Coulometers. (*Voltameters.*) As has been shown, the quantity of electricity passing through any electric circuit can be ascertained by determining the amount of chemical change produced at an electrode surface. An electrolytic cell, so arranged as to measure the quantity of electricity which has passed through it by the amount of chemical action it produces, is called a *coulometer* or a *voltameter*, the former term being preferable. There are three general types of coulometer in use, viz., (1) weight coulometers, (2) volume coulometers, and (3) titration coulometers. These will be considered very briefly in the subsequent paragraphs.

Weight Coulometers. (a) *The Silver Coulometer.* In the weight coulometer, as the name implies, the quantity of electricity is determined by measuring the gain in weight of the cathode plate due to the deposition of metal from the electrolyte. The most accurate of all coulometers is the silver coulometer. This instrument has already been mentioned in connection with the determination of the electrochemical constant (p. 65). The silver coulometer used and recommended by Richards and Heimrod[1] is shown in Fig. 4. It consists of a large platinum crucible E, the inner surface of which constitutes the cathode, a piece of pure silver C, which forms the anode surface, a

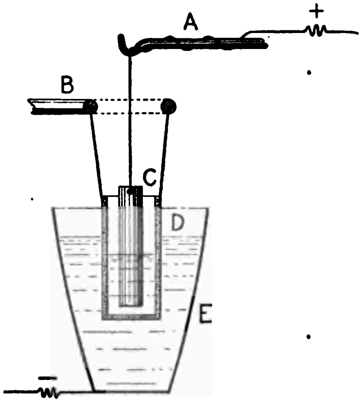

Fig. 4.—Simple silver coulometer.

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[1] Zeit. phys. Chem. *41*, 302. (1902).

porous cup D, to retain any particles of silver which may be detached mechanically by the current, and the glass insulating supports A and B. The electrolyte consists of a neutral solution of silver nitrate, prepared by dissolving 20 to 40 grams of pure silver nitrate in 100 grams of distilled water. By weighing the platinum crucible before and after the passage of the current, the amount of electricity which has flowed through the coulometer may be computed from the electrochemical equivalent of silver, 0.00111800 gram per coulomb. The mean error of a single determination is about 0.03 per cent for a deposit weighing not less than 500 milligrams. The current density must not exceed 0.2 ampere per square centimeter of anode surface or 0.02 ampere per square centimeter of cathode surface. Care should be taken to insure the removal of the last traces of silver nitrate solution before weighing the crucible. This is accomplished by washing with distilled water until the washings give no turbidity with a solution of hydrochloric acid. The crucible is then dried in an air bath and weighed. The solution of silver nitrate may be used repeatedly until a deposit corresponding to 3 grams of silver per 100 cc. of solution has been reached.

A simple and inexpensive form of silver coulometer has recently been designed by the United States Bureau of Standards[1] for general use. The following description of the apparatus is taken verbatim from the official publication.

"The anode was made in the form of a large ring set in a glass dish containing the electrolyte. This silver ring was made large to minimize the difficulties with the anode slime. The cathode was a small platinum ring resting in a shallow glass dish submerged in the electrolyte and so arranged that the whole might be lifted out together. As this platinum ring weighed only 10.5 g., the largest item of expense was reduced to about one-tenth that of the large size standards." It is not intended that this form should be used in any work requiring the highest precision, but it has been shown that it may be relied on to a few hundredths of 1 per cent. The arrangement of the parts is shown in the accompanying drawing (Fig. 5).

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[1] Bull. Bureau of Standards. Vol. 10. p. 529.

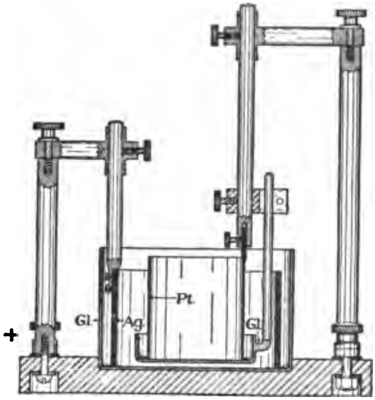

Fig. 5. — Silver coulometer recommended by U. S. Bureau of Standards.

(b) *The Copper Coulometer.* In this instrument the anode surface usually consists of two sheets of pure copper with a thin sheet of platinum or copper between them serving as the cathode surface. The electrolytic solution recommended by Oettel[1] for the copper coulometer has the following composition:

Crystallized Cupric Sulfate	15 grams
Conc. Sulfuric Acid (Sp. Gr. 1.84)	5 grams
Alcohol 95 per cent	5 c. c.
Distilled Water	100 c. c.

When the current density is so adjusted that it does not exceed 0.015 ampere per square centimeter of cathode surface, it is claimed by Oettel that the copper coulometer will give results which agree perfectly with those obtained with the silver coulometer. It has been shown, however, that there are several inherent defects in the copper coulometer which render it a less trustworthy instrument than the silver coulometer. Thus, the copper deposited at the cathode surface dissolves slightly in acid cupric sulfate forming a cuprous salt, thereby diminishing the weight of the cathode plate. If a neutral solution of cupric sulfate be used, there is too great a gain in the weight of the cathode plate owing to the deposition of cuprous oxide resulting from the hydrolysis of cuprous sulfate. As the temperature rises the proportion of cuprous ions to cupric ions increases, causing too great an increase in the weight of the deposit. To reduce errors due to oxidation it is often recommended that a slow current of carbon dioxide be bubbled through the solution. The mean error of a single determination with the copper coulometer is about 0.2 per cent. The advantages of the copper coulometer over the silver coulometer are that it is cheap and that the copper deposit is more adhesive than the silver deposit. A satisfactory form of copper coulometer is shown in Fig. 6.

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[1] Chem. Zeit. *17*, 543 (1893).

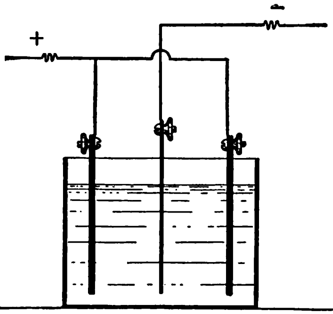

Fig. 6.— Copper coulometer.

Volume Coulometers. The best known coulometer of this type is the so-called water-coulometer. In this instrument the total volume of electrolytic gases, or the volume of either one or the other of the constituent gases of water, is measured. The form of water-coulometer devised by F. Kohlrausch[1] is shown in Fig. 7. A glass tube graduated into 1/10 cc. serves to measure the volume of the gases evolved by the passage of the current thru water which has been made conducting by the addition of sulfuric acid. The graduated tube is fitted into a shallow glass reservoir of about 500 cc. capacity by means of a ground joint. Thru two tubulures, fitted with rubber stoppers, electrical connection is established with two platinum plates. A small thermometer is sealed into the upper part of the graduated tube to enable the experimenter to determine the temperature of the gas. Kohlrausch recommends that a solution of sulfuric acid, sp. gr. 1.14, be used to fill the tube and the reservoir. When the electric current to be measured is passed thru the solution, the uncorrected volume of the resulting mixture of hydrogen and oxygen is read directly on the graduated tube. By means of suitable tables the reduction of the volume of the gas to standard conditions may be readily performed, and, knowing that 1 coulomb of electricity liberates 0.17403 cc. of hydrogen and oxygen

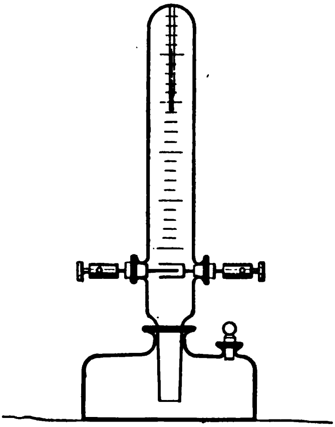

Fig. 7.—Volume coulometer of Kohlrausch.

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[1] Elektrotech. Zeit. *6*, 190. (1885).

in molecular proportions at 0° and 760 mm. pressure, the quantity of electricity which has passed thru the circuit can be easily computed. The convenience in reading the volume of gas corresponding to the current which passes thru the coulometer is offset by the disadvantage that a comparatively high voltage is required. Furthermore, the water coulometer is not adapted to the measurement of large quantities of electricity.

Titration Coulometers. In the measurement of small quantities of electricity the titration coulometer is often useful.[1] The apparatus is shown in Fig. 8. The vertical glass tube, fitted at its lower end with a glass stop-cock, is filled up to the dotted line with a concentrated solution of potassium iodide acidified with hydrochloric acid. A dilute solution of hydrochloric acid is then added by means of a funnel or pipette, care being taken to avoid mixing with the more dense solution. The anode plate consists of a spiral of platinum wire while a piece of platinum foil serves as the cathode plate. When a current of electricity passes thru the solution, iodine is liberated at the anode, 1 equivalent or 126.92 grams of iodine corresponding to 96500 coulombs of electricity. The amount of iodine

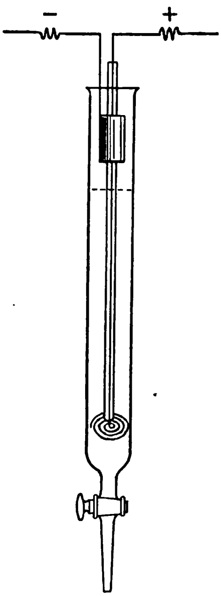

Fig. 8.—Titration coulometer.

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[1] See Danneel, Zeit. Elektrochem. *4*, 154 (1898). See also Washburn and Bates, Jour. Am. Chem. Soc., *34*, 1341 (1912).

set free is determined by withdrawing the lower layer of the solution by means of the stop-cock and titrating with a standard solution of sodium thiosulfate according to the well-known procedure of volumetric analysis.

Section VI

THE ELECTRONIC THEORY

Electric Discharge in High Vacua. The recent advance in our knowledge of the nature of electricity and of the constitution of matter is due in large measure to the pioneer work of Sir William Crookes on the phenomena of electric discharge in high vacua. In a paper communicated to the Royal Society in 1879, Crookes showed that when an electric discharge is passed through a highly exhausted glass tube, rays are shot off from the cathode. These "cathode rays," as they are called, are capable of exciting fluorescence where they impinge upon the walls of the tube; a vivid green fluorescence being developed in soda glass, and a blue fluorescence in potash glass.

The rays travel in a rectilinear path and may be brought to a focus by means of a concave cathode. When various minerals are placed at the focus within the exhausted tube they are rendered fluorescent, while a piece of platinum foil can be rendered incandescent by prolonged bombardment by the rays.

It was Crookes' view that the rays consist of a stream of electrified molecules of the residual gas. In order to test the correctness of this hypothesis he caused the rays, after leaving the cathode, to pass thru two parallel slits cut in an aluminum diaphragm, thus giving two parallel streams of cathode rays. By means of a phosphorescent screen placed within the tube in such a position as to be grazed by the rays, their path could be easily traced. It was found that the two streams of cathode rays diverged; that is, they behaved like two adjacent streams of similarly electrified bodies. From these experiments, Crookes was led to consider these rays as made up of "a fourth or radiant state of matter." Later experiments by Perrin and Sir J. J. Thomson, in which the rays were subjected to the action of both magnetic and electrostatic fields, have proved the rays to consist of negatively charged particles.

Velocity of the Cathode Particle. The velocity of the cathode particle was determined by Thomson in the following manner: The amount of magnetic deflection produced by subjecting the cathode stream to the action of a magnetic field is proportional to the velocity, v, with which the particles are moving, to the intensity of the magnetic field, H, and also to the magnitude of the charge, e, resident upon each particle. The corresponding deflection produced by an electric field is proportional to the intensity of the field, X, and to the charge, e, on each particle. Thomson devised an experiment in which the cathode stream could be subjected to the simultaneous action of both magnetic and electrostatic forces, but so arranged that the effect of one field could be exactly counterbalanced by that of the other, thus causing the cathode stream to pursue an undeviated, rectilinear path. A suitable phosphorescent screen served to detect any deviation from the normal path of the particles when uninfluenced by either magnetic or electric forces.

When the magnetic and electric forces are thus balanced, we have

$$Hev = Xe$$

or
$$v = \frac{X}{H}$$

By means of this equation, the velocity of the cathode particle may be calculated, and it was found that in a highly exhausted tube this velocity may be as high as 60,000 miles per second, or nearly one-third of the velocity of light.

Ratio of Charge to Mass. Thomson next directed his attention to the determination of the ratio which the electric charge carried by a cathode particle bears to its mass. He showed that this ratio can be found by subjecting the rays to the action of an electrostatic field alone. Under these conditions the cathode particles are deflected from their rectilinear path in exactly the same way that a rifle-bullet is deflected from a horizontal path and constrained to fall to the earth at a continually accelerated rate under the influence of the attraction of gravitation.

In the case of a cathode particle, its acceleration will be directly proportional to the strength of the field, X, to its charge, e, and inversely proportional to its mass, m. Or, expressing these facts in mathematical language, we have

$$\text{Acceleration} = \frac{Xe}{m}$$

The science of Mechanics teaches, that the distance thru which a body will fall freely under the influence of gravity in a time t, is $1/2\ gt^2$, where g is the acceleration due to gravity. Similarly, the deflection of the cathode stream under the influence of the electrostatic field, X, as shown by the displacement of the luminous spot on the phosphorescent screen, will be

$$d = \frac{1}{2} \cdot \frac{Xe}{m} t^2$$

Since $t = l/v$, where t, l, and v denote time, distance, and velocity respectively, we may replace t^2 in the above expression for displacement by l^2/v^2, when we have

$$d = \frac{1}{2} \cdot \frac{Xel^2}{mv^2}$$

or

$$\frac{e}{m} = \frac{2d\ v^2}{X\ l^2}$$

In this last equation all of the terms on the right-hand side of the equality sign are susceptible of direct measurement.

Thomson found that the ratio e/m is the same for all cathode rays provided they are not moving with velocities of the same order of magnitude as the velocity of light. He also found that the ratio is independent of the nature of the residual gas in the tube and likewise of the chemical nature of the electrodes. The value of e/m, expressed in electrostatic units, is 5.1×10^{17}. The largest value of e/m hitherto known was that for the hydrogen ion in electrolysis, where the ratio of charge to mass, expressed in electrostatic units, is 3×10^{14}. Therefore, for the cathode particle, the ratio is 1700 times greater than the corresponding ratio for the hydrogen ion in electrolysis. It is evident that this may be due to the charge being 1700 times greater than the charge on the hydrogen ion in electrolysis (the mass of the ion and that of the cathode particle being assumed equal), or, to the mass of the cathode particle being only 1/1700 of the mass of that of the hydrogen ion (the charges being assumed the same).

Magnitude of the Charge, e. It is a familiar fact that fogs are due to the condensation of water vapor on dust particles in the atmosphere, each particle of dust acting as the nucleus around which a droplet of water can form. On cooling a mass of air which has been completely freed from dust, no fog will be formed because there are no nuclei upon which water vapor can condense. Air in this condition is said to be "supersaturated," i.e., it holds more than the normal amount of moisture for that particular temperature. If a little dust be introduced into supersaturated air, an immediate condensation to fog occurs. It has been shown by C. T. R. Wilson that if a vessel be filled with air from which all dust particles have been removed by filtration through cotton-wool, it is possible to cool it to such an extent that it will hold in suspension fully eight times the amount of water vapor it should normally contain. On further cooling, the moisture precipitates in the form of rain.

Wilson also discovered that cathode particles serve as nuclei for the condensation of moisture from supersaturated air, and that condensation occurs at a temperature corresponding to a fourfold saturation. By enclosing a mass of dust-free air in a glass chamber closed by a piston, the desired degree of supersaturation can be obtained by withdrawing the piston, thus expanding the air and lowering its temperature. If cathode rays are then permitted to enter the chamber, a fog immediately results, and by proper adjustment of the expansion, it is possible to estimate the actual weight of water condensed.

Having determined the total weight of condensed moisture, it is evident that a knowledge of the average volume of a single drop would make possible the calculation of the total number of drops, and, on the reasonable assumption that each drop is associated with but one cathode particle, the number of such particles would be known. The volume of a single drop can be computed by means of a formula derived by Sir George Stokes for the velocity of fall of a minute spherical body in terms of its radius, r, and the viscosity, η, of the medium in which it falls. Stokes' formula is

$$u = \frac{2}{9} \cdot \frac{gr^2}{\eta}$$

where u denotes the velocity of fall of the body and g is the acceleration due to gravity. By noting the velocity with which the fog settles in the expansion chamber, the value of r in the foregoing formula may be calculated.

Having calculated the total number of cathode particles, by dividing the total weight of water condensed by the volume of a single drop, $4/3\ \pi r^3$, it only remains to measure the total quantity of electricity on the precipitated water vapor in order to ascertain the charge on each particle. The charge on a single cathode particle was thus found to be 3.1×10^{-10} electrostatic units. Recent improvements in Wilson's method have enabled Millikan[1] to determine the value of e with extreme accuracy. Millikan assigns to e the value 4.4775×10^{-10} electrostatic units, the error not exceeding 1 part in 1000.

These cathode particles were at first called *corpuscles* but they are now commonly known as *electrons.* The electron appears to be nothing but an isolated charge of negative electricity. All electrons are alike, being entirely independent of the particular atom from which they may have escaped. This leads to the view that electricity, like matter, is made up of discrete particles analogous to atoms. An electron may be defined as a minute particle having an apparent mass of about 1/1700 that of the atom of hydrogen and carrying a negative charge of electricity equal to 4.4775×10^{-10} electrostatic units.

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[1] Millikan, Phil. Mag. IV, *19*, 209 (1910); Phys. Rev. *32*, 349 (1911); Trans. Am. Electrochem. Soc., *21*, 185, (1912).

Other Sources of Electrons. Cathode rays are not the only source of electrons. Electrons are given out by radio-active substances, by metals, and by some amalgams when heated or exposed to light, especially to ultra-violet light, and also by gas flames charged with the vapors of salts. Whatever the source from which the electrons may be derived, the value of the ratio, e/m, remains constant. The constancy of this ratio led Sir J. J. Thomson to say that the electron is to be regarded "as one of the bricks of which atoms are built up."

Structure of the Atom. According to Thomson, the atom of any element is assumed to consist of an assemblage of negatively charged particles or electrons, held together by a positively charged nucleus, the amount of positive electricity being equivalent to the total negative charge of the electrons. At the present time little definite information exists as to this positive nucleus, beyond the fact that carriers of positive electricity possess masses which are comparable with the mass of the atom of hydrogen. A small number of electrons near the surface or outer shell of the atom are believed to possess a greater degree of freedom and to be less firmly held than those nearer the positive nucleus. These electrons are known as the *valence electrons*, since their number determines the maximum valence of the atom.

While further discussion of atomic structure lies beyond the scope of this book yet mention should be made of the recent theory of Nicholson.[1] According to Nicholson the positive residue of the atom exists in the form of separate masses, each of uniform density and having diameters which are relatively small in comparison with the diameters of the electrons. Nicholson says, "In a complex atom, built up of simpler systems, the assemblage of positive charges is in many respects similar to the assemblage of electrons which revolve around them, and it is not unlikely that many of the positive charges would also revolve. But they are not all of the same size, although the difference in size is not great. Their mass is so great that a disturbance which could expel one of them from an atom would also expel many of the attendant electrons, and it would be impossible to isolate a positive charge."

The Electron and the Chemical Elements. While the hypothetical atom of Thomson undoubtedly bears but a remote resemblance to the real atom, and while as Thomson has pointed out, there are many imperfections in his theory, it nevertheless sheds a most interesting light on the mutual relationships of the chemical elements and their differences in valence or combining power.

Thomson has calculated the possible distribution of negative electric charges within a sphere of positive electricity of uniform density. When the presence of only one electron is assumed, it necessarily goes to the center of the sphere. Where a larger number are assumed to be present the calculation has been confined to those cases in which the electrons lie in a plane passing thru the center of the sphere. The maximum number of electrons which can be in equilibrium in a single ring is 5. In order to increase the number of electrons in a ring it is necessary to place some of them within the ring. Thus, though a ring containing 6 equally spaced electrons is unstable alone, it immediately acquires stability if 1 electron is placed at the center of the ring. A system involving a greater number of electrons will arrange itself in a series of concentric rings, the number of electrons in successive rings decreasing as the center is approached. The accompanying table shows the numbers of electrons from 1 to 69, arranged in rings, the first line showing the numbers which may fall into one ring, the second line the numbers which may give rise to two rings, the third line those which form three rings, and so on.

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[1] Nicholson, Phil. Mag. IV, *22*, 864 (1911).

NUMBERS OF ELECTRONS IN CONCENTRIC RINGS

1	2	3	4	5

5	6	7	8	8	8	9	10	10	10	11
1	1	1	1	2	3	3	3	4	5	5

11	11	11	12	12	12	13	13	13	13	13	14	14	15	15
5	6	7	7	8	8	8	8	9	10	10	10	10	10	11
1	1	1	1	1	2	3	3	3	3	4	4	5	5	5

15	15	15	16	16	16	16	16	16	16	17	17	17	17	17	17	17
11	11	11	11	12	12	12	13	13	13	13	13	13	14	14	15	15
5	6	7	7	7	8	8	8	8	9	9	10	10	10	10	10	11
1	1	1	1	1	1	2	2	3	3	3	3	4	4	5	5	5

17	18	18	18	18	18	19	19	19	19	20	20	20	20	20	20	20	20	20	21	21
15	15	15	15	16	16	16	16	16	16	16	16	16	17	17	17	17	17	17	17	17
11	11	11	11	11	12	12	12	12	13	13	13	13	13	13	13	14	14	15	15	15
5	5	6	7	7	7	7	8	8	8	8	8	9	9	10	10	10	10	10	10	11
1	1	1	1	1	1	1	1	2	2	2	3	3	3	3	4	4	5	5	5	5

It will be observed that the numbers in the same vertical columns of the table are repeated in each series, the number of electrons in the outer ring forming the top line. For example, in the first column of the first series, we find the numbers 5, 1; in the next series we find the numbers 11, 5, 1; in the next series we find the numbers 15, 11, 5, 1; and in the last series we find the numbers 17, 15, 11, 5, 1.

The bearing of this table on the natural grouping of the chemical elements may be illustrated by considering the properties of all configurations having 20 electrons in the outer ring. The smallest number of electrons in a system having 20 electrons in the outer ring is 59. In this case the number of electrons within is only just sufficient to impart stability to the ring, any slight disturbance being able to cause the loss of 1 electron. Should this occur the residue would acquire a positive charge and the resulting atom, containing 58 electrons, would resemble in its properties a univalent positive element. When we pass from 59 to 60 electrons, the outer ring acquires greater stability owing to the presence of an additional electron within the system. Similarly, the system containing 61 electrons is even more stable than that containing 60 electrons. The stability continues to increase until the number of electrons in the atom reaches 67, when the addition of another electron destroys the stability of the system, since it enters the outer ring, thus increasing the number of electrons to 21, and producing a configuration favoring the detachment of an electron, as in the case of the system containing 59 electrons.

It will be observed that the change from 59 to 67 electrons, produced by the successive additions of a single electron, corresponds to the addition of 8 negative charges. The system containing 60 electrons will be the most positive of the series. It can give up 1 electron, but only 1, since if it were to give up 2, a system of 58 electrons would result, similar to that obtained by the removal of an electron from an atom containing 59 electrons. Such a system would acquire two positive charges of electricity and would possess even greater attraction for external electrons. Therefore, since the atom containing 60 electrons can carry but one positive charge it will resemble in its behavior a univalent positive element.

Turning our attention now to the system containing 67 electrons, we find that the outer ring is very stable, and, as we have seen, the addition of 1 electron would involve a rearrangement resulting in a system having 21 electrons in the outer ring. Since 68 is the minimum number of electrons which can exist under these conditions with an outer ring of 21, it follows that an electron may readily be lost. The resulting configuration of 67 electrons, after thus acquiring a negative charge, would immediately lose it again, and the system would thus be incapable of retaining any permanent charge. Its behavior is quite analogous to the rare gases which are known to be inactive chemically. The system containing 66 electrons can retain but a single negative charge; for should 2 electrons be added to it, a configuration involving 68 electrons would result, and that has already been seen to lose electrons easily. This system then resembles in its properties a univalent negative element.

Proceeding in a similar manner, successively increasing the number of electrons, we obtain systems corresponding to univalent, divalent, and trivalent, positive elements at one end of the series, and trivalent, divalent, and univalent, negative elements at the other end of the series. This is analogous to the familiar arrangement of the chemical elements due to Mendeléef, shown in part in the following table:

7

He	Li	Be	B	C	N	O	F	Ne
Ne	Na	Mg	Al	Si	P	S	Cl	A

When atoms in which the outer rings have a high stability are brought in close proximity to other atoms in which the electrons are less firmly held, an exchange of electrons may occur. In this interchange the electropositive atoms will acquire a positive charge, and the electronegative atoms a negative charge. The resulting oppositely charged atoms will then unite to form a chemical compound.

The Electronic Conception of Valence. Sir William Ramsay has put forward the following hypothesis[1]: — "Electrons are atoms of the chemical element, electricity; they possess mass, they form compounds with other elements; they are known in the free state, that is as molecules; they serve as the bonds of union between atom and atom." According to this hypothesis, when common salt is dissolved in water and undergoes ionization into $\mathrm{N\dot{a}}$ and $\mathrm{Cl'}$ ions, the $\mathrm{N\dot{a}}$ ion is to be regarded as an atom of sodium minus an electron, and the $\mathrm{Cl'}$ ion as an atom of chlorine plus an electron. That is, the sodium atom may be thought of as a compound of the $\mathrm{N\dot{a}}$ ion with an electron, whereas the $\mathrm{Cl'}$ ion may be regarded as a compound of the chlorine atom with an electron. Ramsay represents the union between sodium and chlorine by the equation

$$\mathrm{ENa + Cl = NaECl}$$

where the symbol E denotes the electron. It is the electron, in other words, that serves as the connecting link between the atoms of sodium and chlorine, — it is another way of representing combining capacity or valence. We may then define the valence of an element as the number of electrons which the element loses or gains to form chemical bonds. The formation of a chemical bond or linkage between two atoms necessarily involves the transfer of an electron from one atom to another, and this transfer imparts a negative charge to the atom which gains the electron, and a positive charge to the atom which loses the electron.

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[1] Ramsay, Jour. Chem. Soc., *93*, 778 (1908).

The Electronic Conception of Conductance. As has been pointed out, conductors of electricity may be conveniently divided into two classes; the metals and carbon forming the first class, and dissolved or fused electrolytes the second class. The mechanism of electrical conductance, whether metallic or electrolytic, may be satisfactorily explained in terms of the electronic hypothesis. Thus, when a difference of potential is established between the ends of a metallic conductor, a stream of electrons immediately begins to flow. This electronic stream constitutes the electric current in the metal and the rise of temperature incident to the passage of the current is to be ascribed to the heat developed by the collision of the electrons with the atoms of metal. Since the electric current is to be regarded as a stream of negatively charged carriers of electricity, we are forced to define the "direction of the current" in a metallic conductor as opposite to that in which the electricity really flows.

In conductors of the second class the ions of the electrolyte carry the current, each kind of ion participating in proportion to its current-carrying capacity. Since in the metallic portion of the circuit, including the electrodes, the current consists of a stream of electrons, it follows that at the electrode surfaces there must be an exchange of electrons between the electrodes and the ions of the electrolyte. This exchange of electrons, commonly called an electrochemical reaction, generally involves only those ions which most readily gain or lose electrons under the conditions. It has been shown in the preceding section that the liberation or solution of one equivalent weight of a substance requires approximately 96500 coulombs of electricity. It is evident that if the number of atoms contained in one gram-atom of an element were known, it would be possible to calculate the number of coulombs carried by one electron. It has recently been shown by Perrin that the probable number of atoms in one gram-atom of an element is 68.5×10^{22}; assuming this number to be correct, we have

$$e = \frac{96500}{68.5 \times 10^{22}} \text{ coulombs}$$

and multiplying by 3×10^9, in order to convert coulombs into electrostatic units, we have

$$e = \frac{96500 \times 3 \times 10^9}{68.5 \times 10^{22}}$$

or

$$e = 4.227 \times 10^{-10} \text{ electrostatic units}$$

On comparing this result with Millikan's value for e, viz., 4.4775×10^{-10}, it will be observed that the agreement is all that could be desired. The electrochemical constant or faraday is thus seen to be equal to the product of the charge on the electron and the number of atoms in one atomic weight of an element.

The following references are given for the benefit of those who may desire to gain more detailed information on various phases of the electronic theory:

"The Discharge of Electricity through Gases," by J. J. Thomson,
"Conduction of Electricity through Gases," by J. J. Thomson,
"Electricity and Matter," by J. J. Thomson,
"The Corpuscular Theory of Matter," by J. J. Thomson,
"Beyond the Atom," by J. Cox,
"Elements and Electrons," by William Ramsay,
"The Theory of Valency," by J. Newton Friend,
"The Nature of Matter and Electricity," by Comstock and Troland.

APPENDICES

Appendix 1

VALENCE

Textbooks and different authorities use both the terms "valence" and "valency" in different ways and sometimes rather vaguely; nor is there agreement as to the precise physical conceptions represented by them. In electrochemistry that which is represented by them has an important significance and they ought to be clearly understood and used with definite meanings. When the numerical value of a valence is unity, as it is with hydrogen and a few other elements, it naturally falls out of the calculations and is thereby lost sight of, but in all other cases it is a very important factor, for when the valence is twice as great in one case as in another, the amount of electricity required to produce the chemical change will be twice as great.

When the chemist refers to the "chemical equivalents" of two elements, the valence has already been taken into account and therefore is not given as an additional factor and is lost sight of. Thus the chemical equivalents of zinc (valence 2) and hydrogen (valence 1) are 65.37 (the atomic weight of zinc) and 2.016 (*twice* the atomic weight of hydrogen) when they are given with reference to zinc; or 32.69 (half the atomic weight of zinc) and 1.008 when stated with reference to hydrogen; the ratios of course are the same in both cases. In these ratios the weights have both been reduced to the same valence, hence the valence need then no longer be stated. The chemist therefore often eliminates the valence by referring directly to the "chemical equivalents"; but in many electrochemical calculations the consideration of the valence as a separate factor so greatly simplifies many of the calculations that it is generally worth while doing so, and it enables a table of equivalents such as the one in this book to be prepared for different valences, thereby often saving the worst parts of the calculations. Those who prefer to use chemical equivalents (in which the valence has already been included) will have to make the electrochemical calculations for hydrogen or some other element, and then by means of the chemical equivalents determine from this the corresponding amount of the element in the problem; this involves a double calculation.

Chemists do not seem to be in agreement either as to whether the same physical conception of valence applies equally well to all branches, like organic chemistry and electrolysis. It is believed by the writer however that the following conception of valence is in substantial agreement with the generally accepted electronic theory, that it can safely be applied at least to all electrochemical reactions, and that when properly used in calculations it will always give the correct results. This conception will greatly simplify many electrochemical calculations, and it is believed will also give a clearer understanding of the reactions. It serves at least as a useful and reliable working tool in electrochemistry independently of whether or not it applies equally well to non-electrolytes or organic chemistry.

Bonds. When two different elements are chemically combined to form a compound, it is convenient to consider the force or affinity which holds them together to be represented by chemical bonds. In electrolytes these bonds, or at least some of them, are of such a nature that they may be broken or created by an electric current. The greater the number of such bonds the greater is the quantity of electricity which is required, hence it is convenient for calculations to specify some unit bond in terms of which their number can be measured and specified.

Unit bond. The faraday. For convenience this unit bond is conventionally assumed to be the one combining a gram-atom of hydrogen (1.008 grams) with other elements, and by experiment it has been found that it requires a passage of 96,494 coulombs of electricity to break or create this unit bond. This quantity or charge of electricity is now by general consent called a faraday and is usually abbreviated to 96,500 coulombs; it may often be more convenient to use its equivalent 26.804 ampere-hours.

In the generally accepted electronic theory it is supposed that each gram-ion carries a charge[1] of this amount thru the electrolyte from one electrode to the other, thereby transmitting the current, as explained in Part II. It is where this charge is received or discharged, namely at the electrodes, that the chemical reactions are apparent. From Faraday's law it follows that in electrolysis this bond has the same value when expressed electrically for a gram-ion of any element, hence it serves well as a unit in terms of which the bonds between elements can be expressed or measured.

Definition of valence. This leads to the definition of valence, which may be said to be the number of these unit bonds which each gram-atom has when in combination with other elements. Or expressed electrically, valence may be said to be the number of charges, in faradays, which each gram-atom then carries. This definition applies at least to electrolytes and is therefore sufficient for electrochemical calculations; it is also believed to be the simplest and most useful conception of valence for use in electrochemistry; whether it applies also to non-electrolytes and to organic chemistry is perhaps still open to controversy."[1]

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[1] "An Enlarged Electron of Practical Size: The Faraday," by Carl Hering, Met. and Chem. Engineering, May 15, 1917, p. 598.

Thus in one gram-molecule of water, H_2O, consisting of two gram-atoms of hydrogen and one of oxygen, there must be two such unit bonds uniting those elements, as each one of the two gram-atoms of hydrogen has one by definition, that is, hydrogen has a valence of 1; therefore the single gram-atom of oxygen must be said to have two such bonds, hence its valence is 2. One gram-molecule of water, 18.016 grams, therefore requires two faradays or 53.6 ampere-hours, to break its two bonds.

A bond always joins two elements, but it may be considered with reference to either of them, as it is in this definition of valence. Thus in the above with reference to the hydrogen there is one bond per atom, hence its valence is 1, but with reference to the single atom of oxygen there are two bonds per atom, hence its valence is 2.

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[1] Alexander Smith in his "General Inorganic Chemistry" gives the following definition: "The valence of the atomic weight of an element is the number of atomic weights of hydrogen, or of some other univalent element, which it combines with or displaces."

J. W. Mellor in his "Modern Inorganic Chemistry" gives the following definition: "The valency of an element is a number which expresses how many atoms of hydrogen, or of other atoms equivalent to hydrogen, can unite with one atom of the element in question."

Ordinarily valences are always whole numbers running from 1 to about 8; elements with valences of 1, 2, 3, etc., are called mono-valent, di-valent, tri-valent, etc.; elements like the noble gases which seem never to combine with any other element are best called non-valent, instead of zero-valent, for reasons given below. Much higher valences have been claimed to exist, as also fractional ones, but it is probably safe to say that neither occur in electrolysis, or at least very rarely.

Non-electrolytic bond. Sometimes a bond joins two atoms of the *same* element; a molecule of hydrogen gas for instance is for good reasons considered to be composed of two atoms combined together, that is, it is diatomic. Molecules of some elements have three or four atoms. Such bonds are also assumed to exist in some compounds as expressed in so-called structural formulas, like the one between the two O's in H-O-O-H for instance. But the writer believes it is safe to say that these bonds have no equivalence in faradays and never seem to enter into any electrochemical calculations; all such calculations for the usual cases seem to agree reliably with experiment when the making or breaking of this kind of bond is ignored; Faraday's law does not refer to them; it is believed to be impossible ever to set free the same element at both electrodes, which would mean breaking this kind of a bond electrically. Hence with our present knowledge it seems safe to consider this kind of bond to differ physically from the one combining different elements, at least to the extent that it may be ignored in electrochemical calculations occurring in practice as far as any equivalent in faradays is concerned. Structural formulas are employed chiefly for compounds which are not electrolytes and therefore not subject to electrochemical calculations.

By using the change of valence based on the usual chemical formulas, instead of the valence itself, as described below, it is believed that no errors will arise in neglecting this kind of bond in electrochemical calculations. In electrolyzing a gram-molecule of water, H_2O, it is well recognized and proved by experiment that it requires two faradays, which means that there were two bonds; yet in the gaseous hydrogen formed there are two atoms to the molecule, hence there must be a bond connecting them; this bond was evidently not included in stating that the valence of hydrogen is 1 and that of oxygen 2, nor is it concluded in the chemical formula for water. Whether it originated during electrolysis or existed in the water is perhaps not yet known, but it is known that it does not enter into electrochemical calculations of this kind.

In a compound consisting of more than two elements, like H_2SO_4 for instance, the current cannot break it into more than two parts, hence one part (one of the ions) must contain several elements, in this case it is SO_4 as the current always breaks the bond between the H_2 and the SO_4 instead of the one between the S and the O_4. It does not necessarily follow from this that the bonds between the S and the O are not electrolytic; they may merely be the stronger of the two; in fact it is said to be possible to break these bonds electrolytically also, obtaining free sulfur.

But the kind of bond joining two atoms of the same element seems to be physically different and is not included among those referred to in this book as being represented by a faraday.

Zero valence. If the valence represents the number of bonds in a combination each of which are equivalent to a faraday, it follows that the elements can have no valence when they are in their free uncombined state as there are then no bonds. That is, the valence of any element in its free state must necessarily be considered to be zero. This term is sometimes applied to those elements like the inert gases which never enter into any combinations, that is, they never have any valences. It is preferable to distinguish between these two cases by saying that the latter are non-valent, as in electrochemistry it is very convenient and sometimes quite necessary to be able to refer to the free or uncombined state of an element as one in which it has a zero valence.

Valence vs. valency. For this and other reasons it is very desirable to make a distinction between the terms valence and valency, which formerly have been used rather indiscriminately, thereby causing confusion. The writer recommends[1] limiting the term "valence" as above described to represent the *number of bonds per atom* which the element has in any specific combination, and to limit the term "valency" to express the *property* which an element has to combine with others in various proportions. Thus copper for instance is then said to possess the property of having a *valency* of 1 and 2; and when combined in the specific combination of cuprous chloride its *valence* is 1, while in cupric chloride its *valence* is 2; and in its free state as metal its *valence* is 0.

Change of valence. Every electrolytic reaction will be found to be accompanied by some changes in the valences; this seems moreover to be a necessary consequence from the above conception that the electric current is always accompanied by the making or breaking of bonds in charging or discharging the ions; it moreover seems to be in entire agreement with the modern electronic theory, explained in Part II. It is the amount of this change of valence and not the valence itself which in all cases is the basis of the quantitative electro-chemical calculations. The valence factor which enters into these calculations is always the difference between the valence before and after the reaction. Calculations are sometimes simplified and easier to understand by basing them on the changes of valence, as shown elsewhere in the examples where both methods are illustrated.

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[1] "Inadequacy and Inconsistency of Some Common Chemical Terms" — Metallurgical & Chemical Engineering, December 1, 1916, p. 649.

As every bond of a gram-atom of any element means that one faraday accompanies the making or breaking of it, one faraday will be required per gram-atom for every unit change of valence. To reduce a valence say from 3 to 2 (as in the reduction of ferric to ferrous sulfate) means going one third toward freeing the element of all of its bonds, that is, toward setting it free. The less the change of valence the less electricity it will require to free a gram of that element or to dissolve it.

In the cases in which elements in combination are set free, their valence has been changed from the one they had in combination to zero, hence in such cases and only in such cases is the change of valence numerically equal to the valence which they had in combination. Faraday's law as usually stated in textbooks therefore applies only to this case, which however is the more usual one. But there are cases in which nothing is set free (see Examples 7, 8, 9, and 10) tho there is always a change of valence, hence to become universal this law should refer to the change of valence and not to the valence alone.

Sign of the valence. To carry out this convenient and useful conception of the change of valence it is sometimes necessary or desirable to designate whether a valence is + or −, that is, whether the respective ions in electrolysis carry positive or negative charges; if positive they will travel with the current and tend to go to the cathode; if negative they will travel against the current and tend to go to the anode. And when set free they give up their charges to the electrode, after which they must necessarily have a valence of zero.

The conception of negative valences will not generally be found described in chemical treatises, as chemists do not as a rule take any notice of the sign of the valence, but it is often of advantage to do so in electrochemistry; the conception of negative valences necessarily follows mathematically and physically from the fact that the charges have different signs. The sign is concerned with the direction of the current or with what might be called the direction of the chemical reaction, that is, whether a reduction or an oxidation (adduction) which are chemical opposites. When the signs become reversed in a reaction they are also important factors in determining the electrical quantities in a reaction, as shown below, but with this exception the signs do not affect the quantities, hence the values given in Table I are applicable as well to + as to − valences.

As every one of these bonds joins two atoms in a combination, it necessarily is positive with reference to one of them and negative with reference to the other. Thus in water, H_2O, when the two bonds are considered with reference to the hydrogen they are positive, but with reference to the oxygen they are negative.

Most of the elements will in electrolysis always go to one particular electrode and never to the other; that is, they always carry a charge of the same sign; hydrogen for instance always carries positive charges and therefore goes to the cathode, while oxygen carrying negative charges always goes to the anode. The valence of hydrogen is therefore always + and that of oxygen always −.

Some of the elements, however, like antimony, carbon, chlorine, nitrogen, etc., sometimes carry positive and sometimes negative charges. Their valences are therefore sometimes + and sometimes −, depending upon the nature of their combination; it is always the same in the same combination, at least in all usual cases. These elements must therefore be considered as having both a reducing and an oxidizing or adducing action, depending on the sign of their valence.

Electrolysis separates a compound or combination of elements into two constituents carrying charges of different signs. The compound in its free state must be considered to have no free charge, that is, a zero valence, it being combined with nothing else. From this it follows that the valences of the constituent elements of a compound multiplied by the number of their atoms, must always add up to zero. Thus in nitric acid, HNO_3, $+1+5-6=0$; or in sulfuric acid, H_2SO_4, $+2+6-8=0$. This is often useful in finding the sign of the valence of one of the constituents when those of the others are known.

A radical as a whole may be said to have a valence; thus SO_4 has a valence of -2, as it must balance with the $+2$ in H_2SO_4.

As illustrations of changes of signs of the valence, sulfur in H_2S has a valence of -2 while in the oxide SO_3 it has a valence $+6$ to balance the $3(-2) = -6$ of the O_3. Hence when the sulfur is adduced or oxidized from the former state into the latter, its change of valence is from -2 to $+6$ which is equal to $+8$, the change of valence being the algebraic difference. If this reaction could be carried out electrolytically it would require 8 faradays per gram atom of sulfur, and not 4 as it would be if the signs were neglected. In this change it must pass thru zero valence, which means its free state.

Another illustration is the adduction or so-called oxidation of methane CH_4 into carbon tetrachloride CCl_4. In the former it seems that the valence ought to be stated to be -4 and in the latter $+4$, hence the change of valence is $+8$ and not zero as it would be if the signs were neglected; the $+$ sign before the 8 means that it was an adduction or oxidation. Or in reducing nitric acid, HNO_3, into ammonia, NH_3, the change of valence of the nitrogen is from $+5$ to -3, the difference being -8, and not 2 as it would be if the signs were neglected; the $-$ sign here means that it was a reduction.

Chemical reactions. In electrolysis the only purely chemical reactions which accompany the current are reductions and oxidations (adductions) in the sense of these terms given below. They are chemically the same kind of a reaction, differing only in their sign or direction; each is the direct opposite or reverse of the other; hence whatever is true of the one, the reverse is true of the other.

Reduction. Chemical reductions, when interpreted according to modern accepted theories, always mean a reduction or *loss* of the valence, whether from $+$ to or toward 0, or from 0 to −, or from + to −. The reduced products always go to the cathode. Reducing hydrogen from water is a reduction of its valence from +1 to 0 for each of the two atoms. When the metals are reduced from their combinations to their free state their valences are always reduced from + to 0. When an element has a + valence in a combination it means that it is in an oxidized state and is capable of being reduced, either toward or to the free state or in some cases even beyond, to a negative valence.

Every lowering of the valence should therefore be embraced in the general term chemical reduction, even tho this is not now customary; it would be more consistent and uniform to do so. When a metal combines with free oxygen, the metal is correctly said to have been oxidized, but the oxygen must be said to have thereby been reduced, as its valence has then been reduced from 0 to −2. This is quite consistent when it is considered that the oxidizing property of the oxygen has thereby been reduced, combined oxygen being a less powerful oxidizing reagent than free oxygen.

In a general way chemical reduction also means the loss of bonds and the loss of a companion element and is therefore an appropriate term which can consistently be extended to include all these features. In the author's opinion it also means a loss of the electric charge, whether positive according to the older conceptions or negative according to the newer ones, provided the conceptions are consistently interpreted, as described below.[1] According to some writers, however, reduction is claimed to be a gain of negative charges; at the present writing there seems to be no definite physical proof, it is a deduction involving some disputed definitions.

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[1] For a more detailed discussion, see article on "Oxidation and Reduction in Physical-Chemistry. Consistency of Terms and Conceptions," in the issue of May 1, 1917, Metal. & Chem. Eng., 1917, page 507 by Carl Hering.

It is conventionally assumed all the world over that electricity, water, and gas flow from their positive, high, or compressed state to their negative, low, or rarified state, as is usually indicated by an arrow; conventionally, therefore, it is the positive charge of electricity which flows in the direction of the arrow; a loss of a charge therefore means that it was a positive charge. According to the older conceptions reduction takes place at the cathode, as it ostensibly does, hence corresponds to a *reduction* or *loss* of the positive charge which that ion carried; after the ion has been set free it has a zero or neutral charge; its positive charge may be conceived to flow into the cathode and pass off as the current.

According to the more modern electronic theory, however, it is the negative electricity which is conceived to flow in the opposite direction, a positive charge being then the result of a loss of negative electrons; a loss of a charge therefore means that it was a negative charge. And according to the modern dissociation theory, before any current is applied and before they reach the electrodes the ions have already been dissociated or ionized, whereby they have received their charges; dissociation means decomposition, hence a reduction of the cation. The true chemical reduction of the cations therefore really took place during this process of dissociation, and as they are then left with a positive charge there has been a *reduction* or *loss* of negative electrons during the actual chemical reduction. The final freeing of an element is not an essential part of reduction;

ferric salts are correctly said to be reduced to ferrous, yet nothing is set free thereby. The final freeing of the dissociated ions is a different and subsequent process, and is not the real reduction.

Hence, whether based on the conventional or on the more advanced conceptions, a chemical reduction in electrolysis always corresponds to a *loss* or *reduction* of electric charges as well as of valence.

In the author's opinion it should be clearly understood that this loss of negative electrons must be regarded as taking place *during* the process of chemical reduction or dissociation, hence when it is said that H in HCl for instance has a free positive charge, it refers only to those atoms of the H which *have been* reduced on being ionized by dissociation; those which are still combined as HCl have no free charges, as the HCl as a combination has no free charges, those of its H and Cl (which are equal) being then combined forming the bond, and their mutual attraction may be said to constitute the force which binds the elements to each other; equal and opposite charges always result in electrical neutrality.

As neither the free H nor the undissociated combination HCl as such, has any free charge, there can be no loss or gain of *free* charges during the oxidation of H to HCl; the charges which the H and Cl gain and lose when they combine are equal and opposite, hence neutralize each other. It is therefore wrong, in the author's opinion, to say that *because* the H in HCl is usually (and correctly) marked with a + sign above it, indicating that it has a positive charge, it got this charge when it was oxidized by combining with the Cl. It really got this free positive charge when it was thereafter reduced again by dissociation; the indication of these charges therefore applies correctly only to the dissociated compounds and not to those elements which are still undissociated.

Oxidation or adduction. Chemical oxidation, when interpreted according to modern accepted theories, always means an increase or *gain* of the valence, whether from − to or toward 0, or 0 to +, or − to +. The oxidized products always go to the anode. Oxidation of course is independent of whether the element, oxygen itself is involved or not. Altho by general consent the term oxidation has been extended to include combinations with other elements also, Cu + Cl = CuCl being called an oxidation, yet it is thought by some prominent chemists that a less confusing and a more consistent and appropriate term would be desirable; among all those suggested the best seems to be "adduction,"[1] as the prefix "ad-" implies addition to the valence, bonds, elements, and charges, as explained above in the reverse sense for reduction, the prefix "re-" implying a reduction of them; each is then the exact reverse of the other. This term adduction has been adopted in this book as preferable to oxidation.

What was said above concerning reduction therefore applies in the reverse sense to adduction or oxidation, hence, in the sense explained above, it is always accompanied by a *gain* of valence and negative charges, and in a general sense by a gain of bonds and companion elements.

When an element in combination has a negative valence it means that it is in a reduced state and is capable of being adduced or oxidized to a positive valence, either to or toward the free state or even beyond.

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[1] Suggested independently by Dr. Frederick H. Getman, one of the present authors, but was subsequently found to have been proposed, for similar reasons, by Dr. M. L. Hamlin in a paper by Nelson & Falk, Jour. Am. Chem. Soc., 35, December, 1913, p. 1812.

To combine a free element with oxygen, fluorine, etc., which is called oxidation or adduction of that element (but not of the oxygen), is to increase its valence from 0 to +. But the setting free of sulfur from H_2S for instance is also an increase of its valence from -2 to 0; it must therefore also be considered broadly as an adduction or oxidation, and in H_2S the sulfur must be considered to be in even a more highly reduced state than when free; it can be further oxidized to SO_3 and its valence then becomes $+6$. It is also exactly the same process as setting free oxygen from an oxide, as the valence of the oxygen has thereby been increased from -2 to 0; it would seem to be preferable to call this "adduced oxygen" rather than "oxidized oxygen;" such free oxygen has a greater oxidizing power than when combined, this power having been added to or increased; the inconsistency lies in the terms and not in the physical facts.

In the case of cuprous chloride, CuCl, the chlorine has a negative valence and at the anode it tends to be adduced or oxidized to its free state. In that case its adducing or oxidizing power has been increased and therefore it tends to adduce or oxidize some of the remaining CuCl to the cupric salt $CuCl_2$ (see Example 10).

Numerical values of the valences. The valences which the elements have in their different compounds are given above in Table IV revised for this book by the kindness of Dr. Jos. W. Richards. The signs which these valences have are included in each case. The table gives what he calls the "practical valences," that is, the actual ones irrespective of any interpretation involving what are called structural formulas.

Some of the elements, like hydrogen, silver, zinc, oxygen, etc., practically have only one valence in all their usual combinations, hence they each have but one electrochemical equivalent; but some other elements, like copper, iron, nitrogen, etc., may sometimes have one valence and sometimes another, hence they have several electrochemical equivalents. With some of the latter the electrochemical reaction merely changes the valence from one of its values to another, in which case they may have still another equivalent corresponding to this change; with iron, for instance, there can be a change of valence of 1, yet it never has this valence. With most of the elements the sign of the valence is either always + or always −, in all their compounds, but with some of them, namely antimony, arsenic, bromine, carbon, chlorine, iodine, nitrogen, phosphorus, selenium, silicon, sulfur, and tellurium, the valences are sometimes + and sometimes −, tho always the same in the same combination, at least in all usual cases.

In the usual electrolytes (tho rare exceptions are claimed to exist) the following general rules may be of service: The valence of hydrogen is always $+1$ (tho perhaps $+2$ in H_2O_2), oxygen always -2, chlorine in chlorides -1, SO_4 in sulfates -2, NO_3 -1, ClO_3 -1; in metallic solutions in which the metal is the base, the valence of the metals is + and that of the radical −.

As described above, when the valences are given their proper signs and when multiplied by the number of the atoms of an element, they must always add up to zero in any compound. Thus in nitric acid, HNO_3,

$+1+5-6=0$, or in ferric sulfate, $Fe_2(SO_4)_3$, $2(+3)+3(6-8)=+6-6=0$. As every one of these bonds has a positive and a negative end, the number of the positive ends must of course equal the number of negative ones. This principle may be used to determine the valence and its sign, for one element of a compound when those for the others are known.

The valence of an element can also often be determined by finding the number of hydrogen atoms which will replace that element in an analogous compound. Thus silver has a valence of 1 because in silver nitrate, $AgNO_3$, it replaces one of hydrogen in the analogous compound nitric acid, HNO_3. Or the valence of silicon is 4 because in its oxide, SiO_2, it replaces four atoms of hydrogen in the oxide of hydrogen $2(H_2O)$, when the amount of oxygen is made the same in both; the valence of oxygen is here considered to be the same in both, it being assumed to have only one valence, an assumption which seems to be generally accepted, tho it is sometimes contested.

The valences of the radical or ion SO_4 must be -2 because in H_2SO_4 the hydrogen has a valence of $+1$, hence $+2-2=0$. Knowing the valences of SO_4 to be -2, that of iron in the ferric sulfate $Fe_2(SO_4)_3$ must be $+3$ because $2(+3)+3(-2)=0$.

These simple rules will suffice for most cases occurring in the ordinary and usual electrochemical calculations; there may be some complicated cases in which there is some doubt; in such cases one should either consult a chemist or make the electrochemical calculation by some indirect method by using some other element of which the valence is known, like hydrogen, and then find by purely chemical calculation what the chemically equivalent amount is of this other element in terms of the one involved in the problem. Examples illustrating this method are given in Section IV, altho there is probably no doubt in any of these as to what the valences are.

Strength or intensity of bonds. Each of these chemical bonds in electrolytes represents the same quantity of electricity, namely one faraday, which is the charge carried by a univalent or monovalent gram-ion, and is therefore the same for all the elements, yet what might be called the strengths or intensities of the bonds, measured in terms of the energy which they represent when made or broken, is quite different in different combinations of elements.

As all these bonds are alike in the quantity of electricity which they represent, it follows that the greater the number of these bonds in any combination, that is, the greater the valence, the greater will be the quantity of electricity involved. In this sense the greater the valence the greater the strength or intensity of the total combining power. But quantity of electricity by itself is not energy, hence it does not represent the strength or intensity in the sense of energy; it is only one factor of energy in the same sense that either feet or pounds are only one of the factors of foot-pounds of energy. Coulombs or ampere-hours must be multiplied by volts in order to express the energy. The so-called heat of combination of a chemical reaction (more correctly the energy of combination, as in electrolysis this energy does not appear as heat) truly expresses the energy.

While these unit bonds represented by a faraday are alike for all elements, yet the energy represented by a unit bond may be and generally is quite different for the different elements and even for the same element in different combinations. The true strength or intensity or degree of chemical affinity is better expressed in terms of energy. The energy in joules (the product of the volts and the coulombs) represented by one of these bonds is equal to the faraday expressed in coulombs, namely 96,500, multiplied by the volts required for producing the chemical separation (an endothermic reaction), or by the volts generated by their formation in the case of a battery (an exothermic reaction). For instance, in the decomposition of a gram-molecule of water, H_2O, there are two bonds each representing 96,500 coulombs; if the decomposition voltage is 1.5 the strength of each bond measured in terms of energy is $96,500 \times 1.5 = 144,750$ joules; and as one joule $= 0.000,2778$ watt-hours, this is equal to 40.2 watt-hours. As there are two bonds the total strength is 80.4 watt-hours; this means that it will take 80.4 watt-hours of energy to decompose a gram molecule of water equal to about $2 + 16 = 18$ grams. If the value of the faraday is taken in ampere-hours, namely 26.80, and is then multiplied by the volts (1.5), giving 40.20 watt-hours per bond, the calculation becomes simpler. But great care must be taken in using the correct voltage of decomposition, as other factors enter when it is measured; the voltage here referred to is that determined from the so-called heat of chemical combination usually stated in calories. For monovalent ions the number of volts is equal to this energy of combination expressed in kilogram calories per gram-molecule, divided by 23.061; for multivalent ions this constant must be multiplied by the valence.

For calculations of the energies involved in electrochemical reactions other than those stated in the headings of the columns of Table I, appropriate treatises should be consulted, as this is beyond the intention of the present descriptive remarks on valence.

C. H.

Appendix II

ELEMENTARY PRINCIPLES OF CHEMICAL REACTIONS AND CALCULATIONS

The following brief statements of a few of the elementary principles of chemistry are given here to enable one who is not a chemist to follow more intelligently the chemistry necessarily involved in the electrochemical calculations described in this book. For the less usual kinds of calculations some further knowledge of chemistry may be necessary, while for the more involved problems treatises on chemistry must be consulted. For some of the more complex cases the necessary facts are not yet known, and their explanations are still controversial.

Elements; atoms; molecules; radicals; combinations; subscripts. There are known at present 83 elementary substances, called the chemical elements, which alone or in various combinations with each other constitute all matter; they are all given in Table I, and are generally represented by the symbols given in the second column. For convenience in describing the reactions between these elements and for making calculations, it is assumed that certain extremely small unit particles of them exist, called atoms. Chemical compounds are made up of various combinations of these atoms, and are represented by formulas in terms of their symbols; in a compound the numbers of these atoms in the smallest possible particle of the compound, which is called a molecule, are indicated by subscripts. Thus H_2O means that in this compound two atoms of hydrogen (H) and one of oxygen (O) are combined to form one molecule of this chemical compound, which is water. $CuSO_4$ means that one atom of copper (Cu), one of sulfur (S), and four of oxygen (O) are combined to form one molecule of what is called copper sulfate. Subscripts therefore denote the number of the atoms of any particular element in a molecule. These compounds are formed by the union of these atoms in those proportions, and they may be decomposed again into their elements by breaking this union. Sometimes a fractional part of a molecule is for convenience called a radical, but it does not exist by itself; thus SO_4 is a radical in $CuSO_4$, $ZnSO_4$, $Fe_2(SO_4)_3$. In electrolysis a radical may sometimes be considered to act like an element; thus in the electrolysis of $CuSO_4$ the Cu goes to the cathode and the SO_4 to the anode.

Electrolytes; electrodes. If in their liquid states, either molten or dissolved, these compounds conduct an electric current and are decomposed by it, they are called electrolytes. The passage of a current thru them always changes them chemically in some way (reduction, adduction, or oxidation) at the two places where the current enters and leaves the liquid; these places are at what are called the electrodes; the one thru which the current enters the liquid is called the anode, and the one thru which it leaves, the cathode; this is true whether the current enters from an outside source, as in the case of an electrolytic bath, or whether it is generated internally as in a battery.

Reactions; equations; coefficients. When brought into contact with each other, many of these chemical compounds act in various ways on each other, producing chemical changes; these actions are called chemical reactions; they are generally expressed in the form of an equation showing the constitution of the mixture before and after the reaction. The number of atoms has, of course, not been changed, hence must always be the same on both sides of these equations. The number of molecules of these substances required to produce these reactions is indicated by numbers preceding them called coefficients. Thus

$$3\ Pb + 8\ (HNO_3) = 3\ Pb(NO_3)_2 + 2\ NO + 4\ H_2O$$

means that three atoms of lead, Pb, and eight molecules of nitric acid, HNO_3, will react on each other to produce three molecules of nitrate of lead, $Pb(NO_3)_2$, and in doing so will set free two molecules of nitric oxide gas, NO, and four molecules of water, H_2O; the number of atoms of each kind before and after the reaction will be found to be the same, and, of course, must always be made to be the same in writing out the equation to make it balance. The coefficients 2, 3, 4, and 8 in the above equations indicate the number of molecules involved.

When with the aid of platinum electrodes an electric current is then passed thru a solution of this nitrate of lead, which is an electrolyte, it decomposes this salt into one atom of free lead, Pb, one of oxidized lead, PbO_2, and one of nitric acid, HNO_3. The reactions before and after are then shown by the following equation, which in order that it shall balance must include two molecules of water, H_2O, which also enters into the reaction.

$$2\ Pb(NO_3)_2 + 2\ H_2O = Pb + 4\ HNO_3 + PbO_2$$

Relative weights; atomic, molecular, and formula weights. The *relative* weights of the atoms of the elements, that of oxygen being by convention assumed to be 16, are called the "atomic weights" and are given in column 3 of Table I. Adding together the atomic weights of all the atoms forming a molecule, being careful to note the subscripts (the coefficients are not concerned), gives the so-called molecular weight, or preferably the formula weight, of the whole molecule, and the proportional part of this total weight which is due to any one of the elements, or group of elements, is then easily determined by simple proportion. Thus for nitrate of lead, $Pb(NO_3)_2$, taking the respective atomic weights from the table gives the molecular or formula weight: $207.20 + 2\ (14.01 + 16 \times 3) = 331.22$. The lead forms $207.20 \div 331.22 = .626$ of it (62.6 %) or nearly 2/3; the two parts of the radical NO_3 form the other third; and the six oxygen atoms ($6 \times 16 = 96$) form $96 \div 331.22 = .29$ or nearly 30 % of it.

Actual weights; gram-atoms; gram-molecules; gram-ions. Such atomic weight calculations however give merely relative weights or proportions, but not absolute weights in grams or pounds. In order to get the latter all these ideal diminutive atoms are for convenience supposed to be enlarged the same number of millions of times until the enlarged oxygen atom weighs 16 grams, then all the actual weights of the correspondingly enlarged atoms of all the other elements will be as many grams as is expressed numerically by their atomic weights. These are called gram-atoms or sometimes "one atomic weight;" or when added together for a molecule they are called gram-molecules. They then become tangible quantities which are easily weighed, a gram-molecule of water for instance being about 18 grams, or 18 cubic centimeters; a gram-atom of copper being there is none at all; the stronger affinity will in general overpower the weaker. In electrochemical calculations involving merely the quantities of substances set free or dissolved or changed by a given current, that is, in such as are calculated with the aid of the present tables, this factor of affinity does not enter, as a given current will set free or dissolve the same amount of any one element whether that element is tightly or loosely combined with other elements, provided that the valence is the same. The intensity of this chemical affinity will have an effect on the voltage that is required to bring about the reactions or is produced by it, but it has no effect on the number of coulombs or ampere-hours that are required for electrolyzing a given quantity of the material.

Primary and secondary reactions. In electrolysis the current will produce certain chemical reactions, after which the products produced may react chemically on each other or on some other substance present; the former is called a primary reaction and the latter a secondary one, as it is not produced directly by the current. In the electrolysis of sulfuric acid, H_2SO_4, for instance, the hydrogen is set free at the cathode which is a true primary reaction; but the SO_4 which goes to the anode, cannot exist as such and therefore combines with the hydrogen of the water always present, setting free oxygen at the anode. This latter is sometimes called a secondary reaction, tho on the other hand it may be claimed that the electrolytic process has not been completed until definite compounds have been produced, and not merely radicals. It may also be said that as the amount of sulfuric acid is the same after the reaction as before, while the water diminishes, it was the water and not the acid which was electrolyzed. If the anode is of copper it will be dissolved by the SO_4 ions forming $CuSO_4$, which would seem to be a true primary reaction.

It is sometimes difficult to discriminate between the two reactions; in some cases authorities differ and no generally accepted definitions to distinguish clearly between them seem to exist; but when reactions do not take place exactly simultaneously with the passage of the current and in exact proportion to it, or when they continue after the current ceases, they are unquestionably secondary. The author suggests that in view of the fact that some energy changes are generally involved in all chemical and electrochemical reactions, a primary reaction may be said to be the one whose energy (endothermic or exothermic) appears in the electric circuit, while a secondary reaction is one whose energy does not appear in the electric circuit.

C. H.

Appendix III

CONVERSION FACTORS USED IN ELECTROCHEMICAL CALCULATIONS

Taken from Hering's " Conversion Tables."

Length.

1 centimeter = 0.3937 inch
1 inch = 2.540 centimeters

Surface.

1 sq. inch = 6.452 sq. centimeters
1 sq. decimeter = 15.50 sq. inches
1 sq. decimeter = 0.1076 sq. foot
1 sq. foot = 9.290 sq. decimeters

Volumes.

1 cb. centimeter = 1 milliliter
1 cb. centimeter = 0.06102 cb. inch
1 cb. inch = 16.39 cb. centimeters
1 quart = 1.101 liters
1 liter = 1.057 quarts (U. S.; liquid)
1 liter = 0.2642 gallon (U. S.; liquid)
1 gallon = 3.785 liters
1 gallon = 0.1337 cb. foot
1 cb. foot = 28.32 liters
1 cb. foot = 7.481 gallons (U. S.; liquid)

Weights or Masses.

1 gram = 15.432 grains
1 pennyweight (troy) = 1.555 grams
1 ounce (advp.) = 28.35 grams
1 ounce (troy) = 31.10 grams
1 pound (advp.) = 0.4536 kilogram
1 kilogram = 2.205 pounds (avdp.)

Weights and Volumes.

1 pound per gallon = 0.1198 kilogram per liter
1 kilogram per liter = 8.345 pounds per gallon

Water.

1 liter = 2.205 pounds
1 gallon = 8.345 pounds
1 cubic foot = 62.43 pounds
1 pound = 0.4536 liter
1 pound = 0.1198 gallon
1 pound = 0.01602 cb. foot
1 kilogram = 0.2642 gallon

Energy (heat).

1 joule = 0.2389 gram calorie
1 thermal unit (BTU) = 252.0 gram calories
1 watt-hour = 0.8600 kg. calorie
1 kg. calorie = 3.968 thermal units
1 kg. calorie = 1.163 watt-hours.

Power.

1 watt = 0.2389 gram calorie per second
1 gram calorie per second = 4.186 watts
1 horse-power = 0.7457 kilowatt
1 kilowatt = 1.341 horse-powers

Electrochemical Equivalents in Energy (other than those given in Table I).

$$\left.\begin{array}{ll}\text{Grams per watt-hour} = & 0.0373\times\\ \text{Kilograms per horse-power-hour} = & 0.0278\times\\ \text{Pounds per kilowatt-hour} = & 0.0822\times\\ \text{Pounds per horse-power-hour} = & 0.0613\times\end{array}\right\}\frac{\text{atomic weight}}{\text{change of valence}\times\text{volts}}$$

$$\left.\begin{array}{ll}\text{Watt-hours per gram} = & 26.8\times\\ \text{Kilowatt-hours per pound} = & 12.2\times\\ \text{Horse-power-hours} = \text{per kilogram} = & 36.0\times\\ \text{Horse-power-hours per pound} = & 16.3\times\end{array}\right\}\frac{\text{change of valence}\times\text{volts}}{\text{atomic weight}}$$

Electrochemical energy.

For monovalent ions:

Volts = kilogram calories per gram molecule × 0.0434

For multivalent ions divide the volts thus obtained by the valence

Electrolytic deposits.

1 gram per sq. decimeter	=	0.02048	pound per sq. foot
1 pound per sq. foot	=	48.82	grams per sq. decimeter
1 pound per year	=	0.002738	pound per day (of 24 hours)
1 pound per year	=	0.0008624	gram per minute
1 pound per day (of 24 hours)	=	0.1826	short ton per year
1 gram per minute	=	1160.	pounds per year
1 short ton per year	=	5.476	pounds per day
1 pound per hour	=	4.383	short tons per year (day of 24 hours)

(The year is considered to be $365\frac{1}{4}$ days.)

C. H.

Appendix IV

GLOSSARY

The numbers refer to the pages on which the definitions or explanations will be found.

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